LECTURE SCHEDULE

Mon	(Ke3) 12.15 – 14.00
Wed	(Ke2) 10.15 – 12.00
Fri	(Ke5) 10.15 – 12.00

		Date	Topic
1.	Wed	06.09.	Course Introduction & Short Review on Elements & Periodic Table
2.	Fri	08.09.	Short Survey of Main Group Elements
3.	Mon	11.09.	Zn + Ti, Zr, Hf & Atomic Layer Deposition (ALD)
4.	Wed	13.09.	Transition Metals: General Aspects & Pigments
5.	Fri	15.09.	Redox Chemistry (Ke4)
6.	Mon	18.09.	Crystal Field Theory
7.	Wed	20.09.	V, Nb, Ta & Perovskites & Metal Complexes & MOFs & MLD
8.	Mon	25.09.	Cr, Mo, W & 2D materials & Mxenes & Layer-Engineering
9.	Wed	27.09.	Mn, Fe, Co, Ni, Cu
10.	Fri	29.09.	Cu & Magnetism & Superconductivity
11.	Mon	02.10.	Ag, Au, Pt, Pd & Catalysis (Antti Karttunen)
12.	Wed	04.10.	Lanthanoids + Actinoids & Luminescence
	Fri	06.10.	
13.	Wed	11.10.	Resources of Elements & Rare/Critical Elements & Element Substitutions
14.	Fri	13.10.	Inorganic Materials Chemistry Research

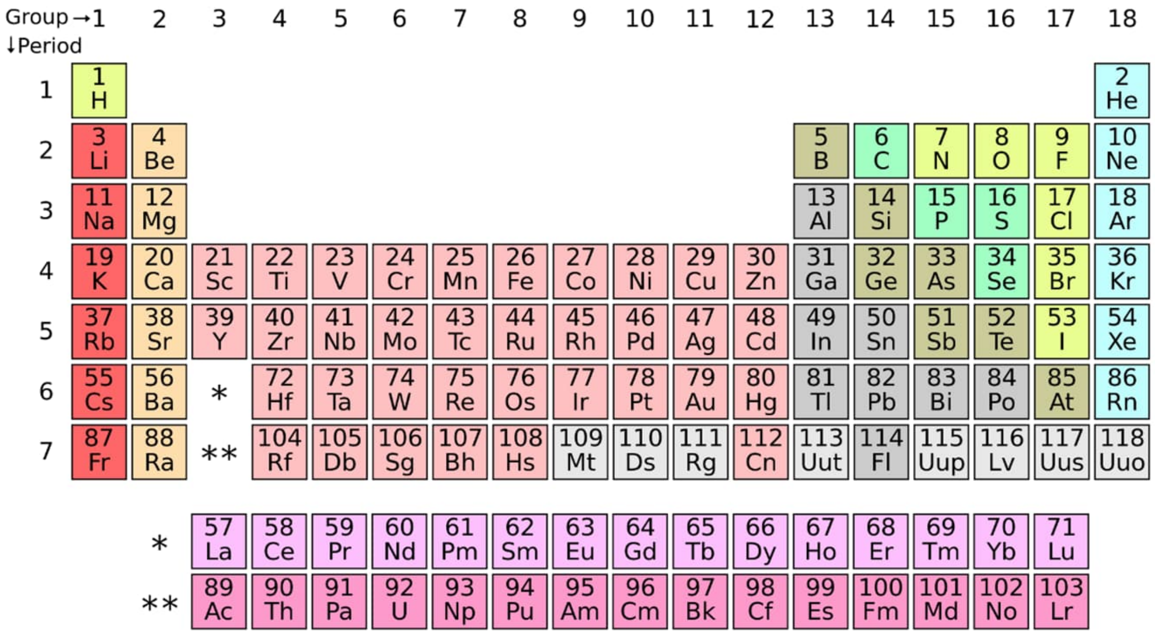
EXAM: Tuesday Oct. 17, 9:00-12:00 in Ke2

PRESENTATION TOPICS/SCHEDULE

Mon	25.09.	Mo:	
Wed	27.09.	Mn:	Naomi Lyle & Sanni Ilmaranta
		Ru:	Miklos Nemeszeghy & Timo de Jonge
Fri	29.09.	Cu:	Koshila Hiruni & Kaushalya Poonanoo
Wed	04.10.	Eu:	Binglu Wang & Maryam Jafarishiad & Saara Siekkinen
		Nd:	Patrich Wiesenfeldt & Tomoki Nakayama
		U:	Miikka Viirto & Ashish Singh
Wed	11.10.	Co:	Gabrielle Laurent & Yan Zheng
		In:	Sonja Alasaukko-oja & Katri Haapalinna
		Te:	Sofia Rantala & Roger Peltonen

QUESTIONS: Lecture 3

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?



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

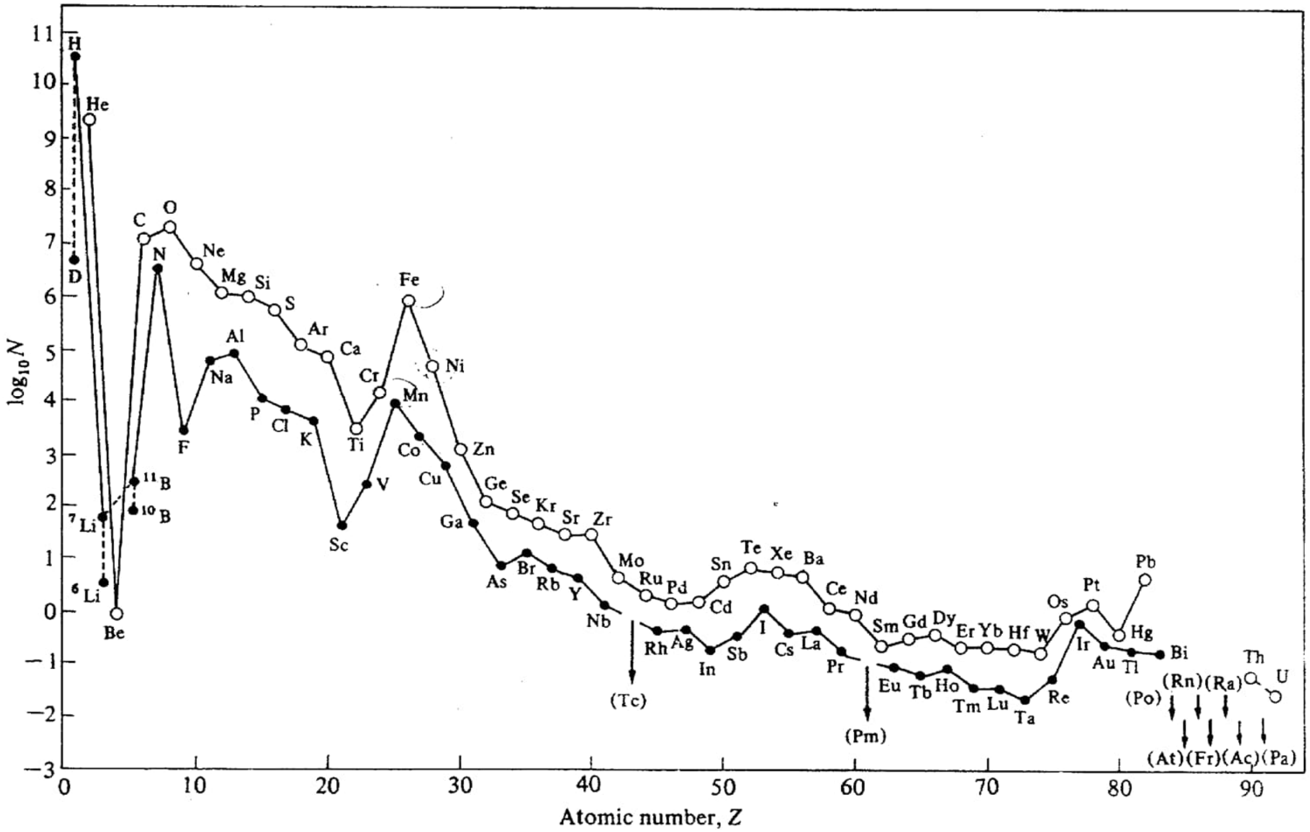
IONIC RADII (in Å): Depending on Coordination Number

		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

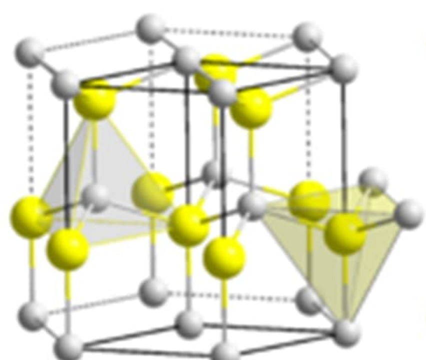
OCCURRENCE of the METALS: Zn, Ti, Zr, Hf

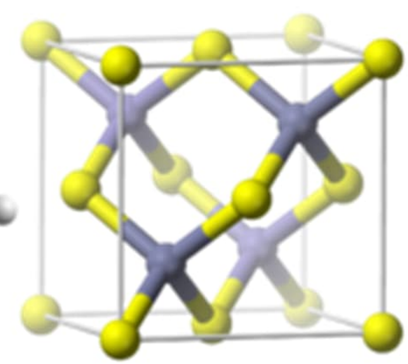
- **Zn** (d^{10}, not transition metal) is the fourth most common metal <u>in use</u> (after Fe, Al and Cu) with an annual production of ca. 13 million tonns
- **Ti:** widely distributed, many minerals (most common rutile and ilmenite)
- **Zr:** found in more than 40 minerals
- **Hf:** quite rare, no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



ZnO

- 4-coordination in hexagonal wurtzite & cubic zinc blende (diamond like) structures
- 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 small excess of zinc/hydrogen → n-type doping
- Al^{3+}-for-Zn^{2+} doping for enhanced n-type doping
- Problem for some applications): p-type doping has not been achieved
- Attractive properties for optoelectronics: wide bandgap, high transparency, tunable electrical properties, high electron mobility → transparent electrodes, liquid crystal displays, energy-saving windows, electronics as thin-film transistors and light-emitting diodes → THIN FILMS





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 (important for evolution)
  - **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** (to be discussed next week): flexible for adjustment of nearest-neighbour surroundings

TITANIUM: Use as a metal / in metal alloys

- **Corrosion resistance: pulp and marine industry, chemical processing, and energy production/storage applications**
- **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

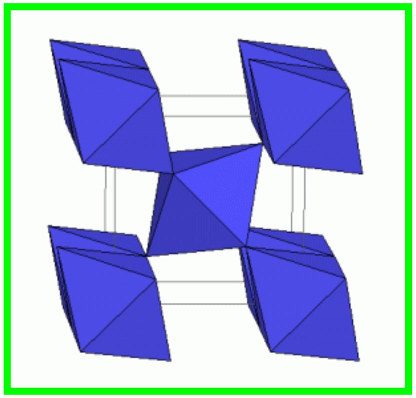
- **Exactly the same size (due to shielding effect/lanthanide contraction)**
- **Of all the 4d-5d transition metal pairs, Zr and Hf are the most similar**
- **Separation of Hf from Zr very difficult**
- **Hf was discovered as late as 1922 (Zr more than 100 years earlier)**
- **Hf was the first element 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 absorption (Hf 600-times stronger): different (opposite) uses in nuclear power plants**

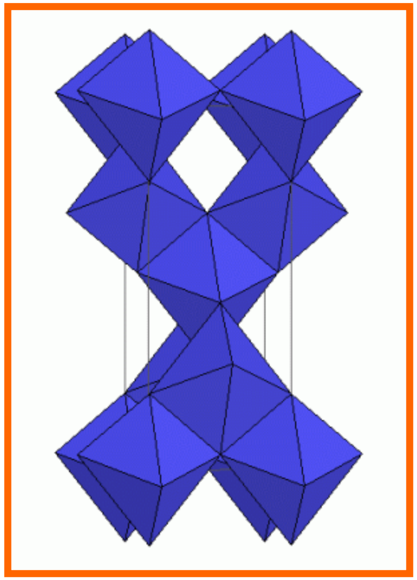
SEPARATION of Zr and Hf

- **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

TiO_2 (important chemical, produced worldwide)

- **Crystal structures:** - rutile, anatase, brokite (6-coord.)
- **White pigment:**
  - large refractive index
  - used in paints, paper, plastics, cosmetics, foods, tooth pastes, …
- **UV protection:** - sunscreens, plastics
- **Inert/non-poisonous:** - 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

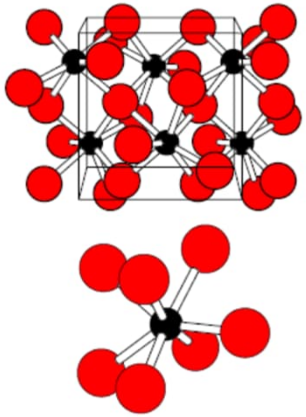




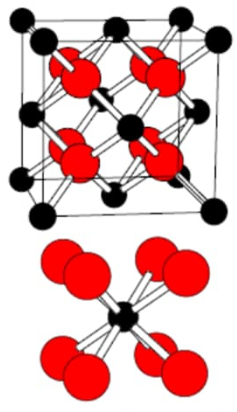
ZrO_2

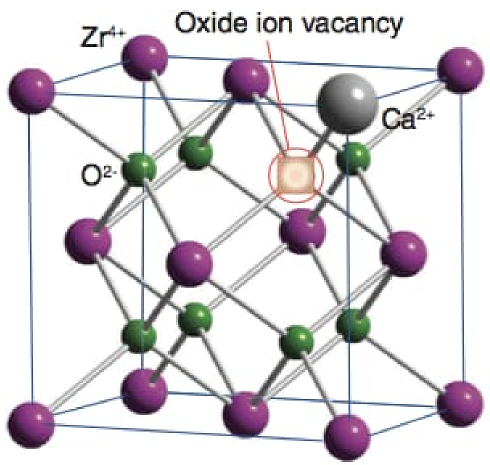
- Used as industrial ceramics, protective coating (e.g. on TiO_2 pigment particles) and refractory material in e.g. insulation
- Monoclinic (7-coord.) structure at RT &
  cubic (8-coord.) structure at high temperatures
- Y^{III}-for-Zr^{IV} substitution stabilizes the cubic ZrO_2 structure
- Yttrium-stabilized 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)

Room Temperature
Monoclinic ($P2_1/c$)
7 coordinate Zr
4 coord. + 3 coord. O^{2-}



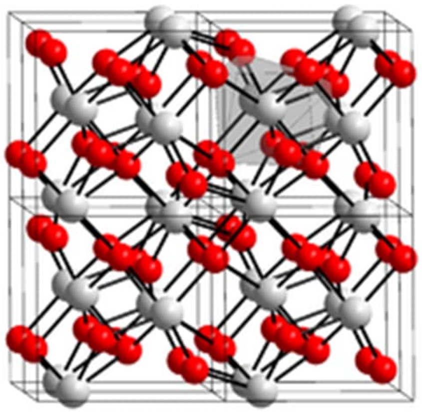
High Temperature
Cubic (Fm3m)
cubic coordination for Zr
tetrahedral coord. for O^{2-}





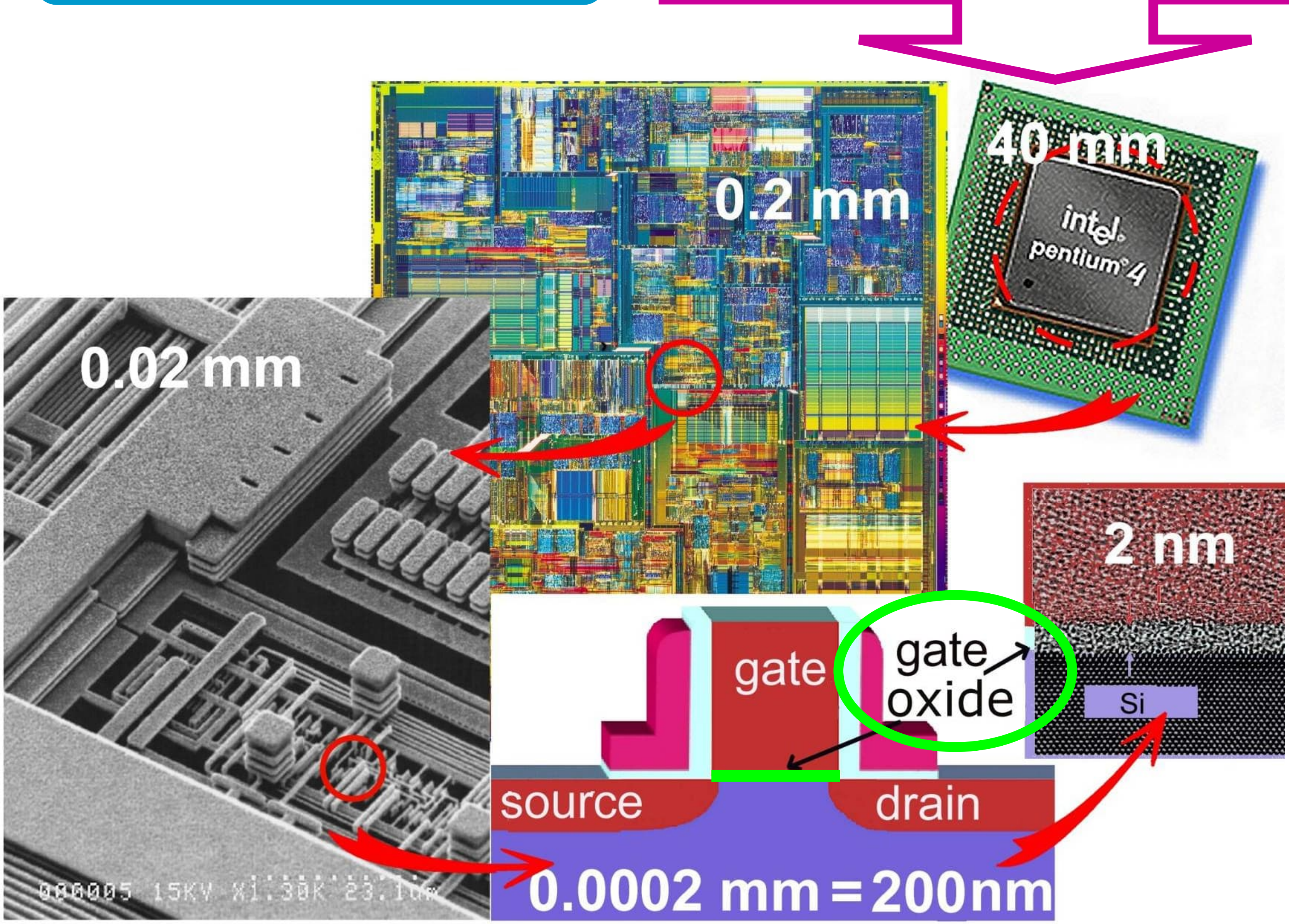
HfO_2

- Similar monoclinic (7-coord.) 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 THIN FILMS using ALD
- Partial substitution of Hf by Si (or Al) increases the crystallization temperature



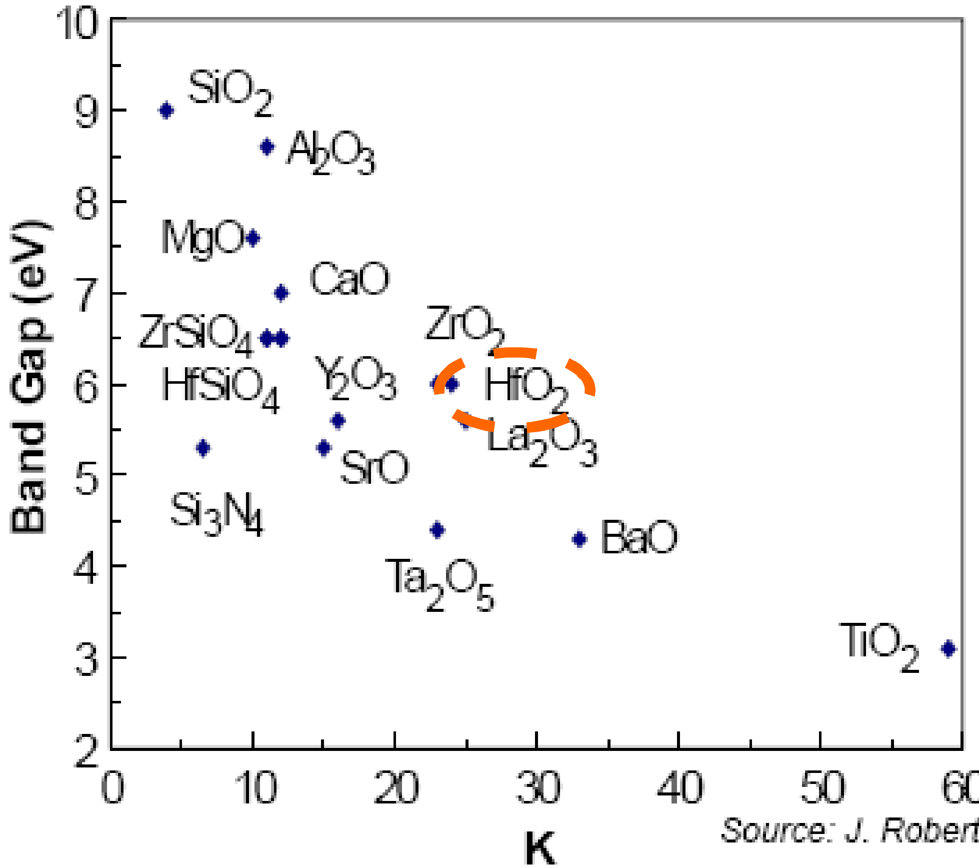
CMOS transistor

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



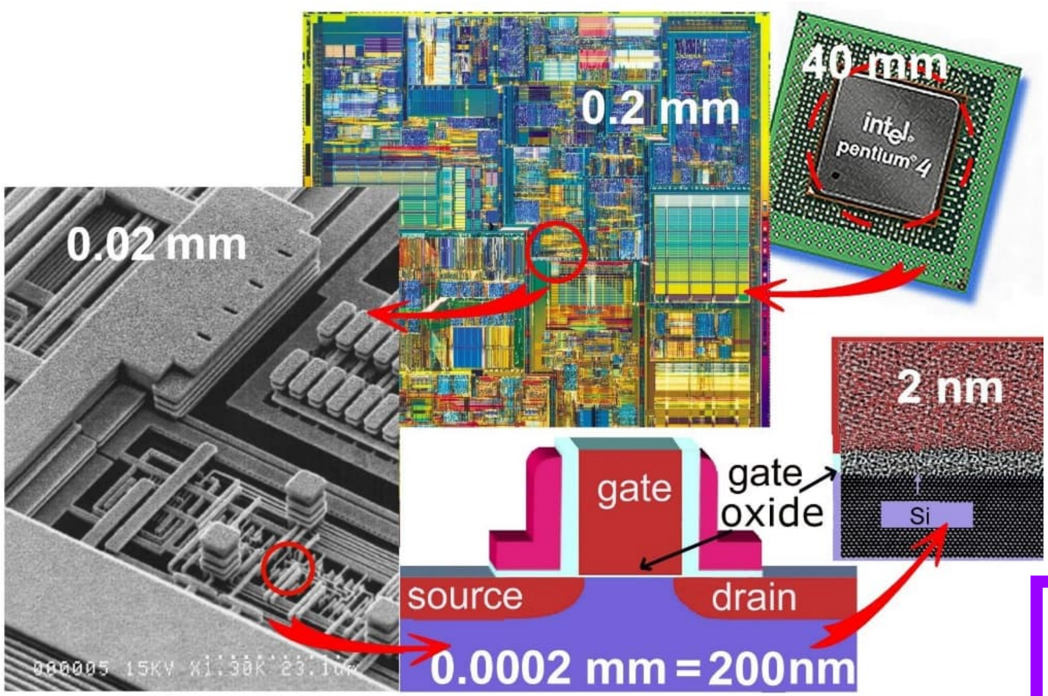
Conditions for high-*k* dielectrics

- 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

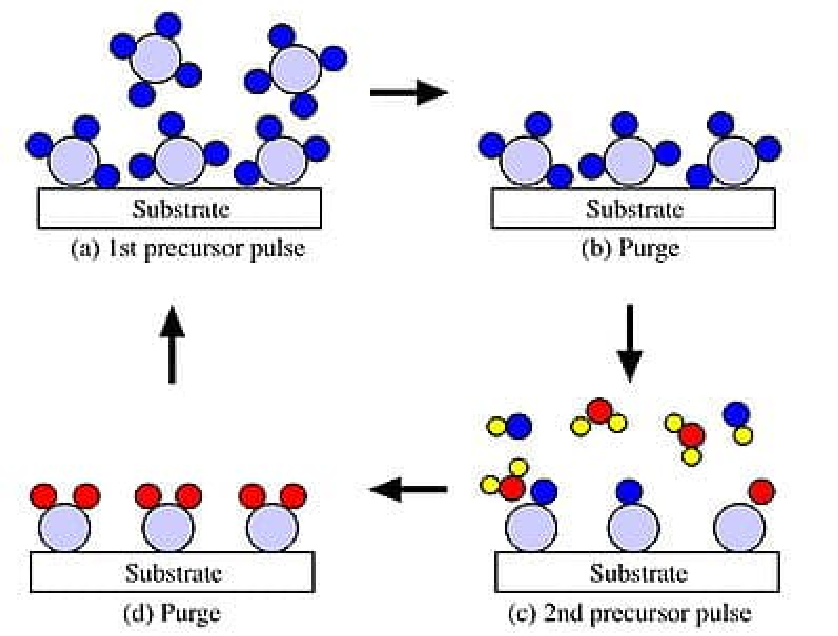


- **High-quality (pinhole-free)**
- **Thickness control (atomic level)**
- **Large-area homogeneity**
- **Conformity → Nanostructuring**

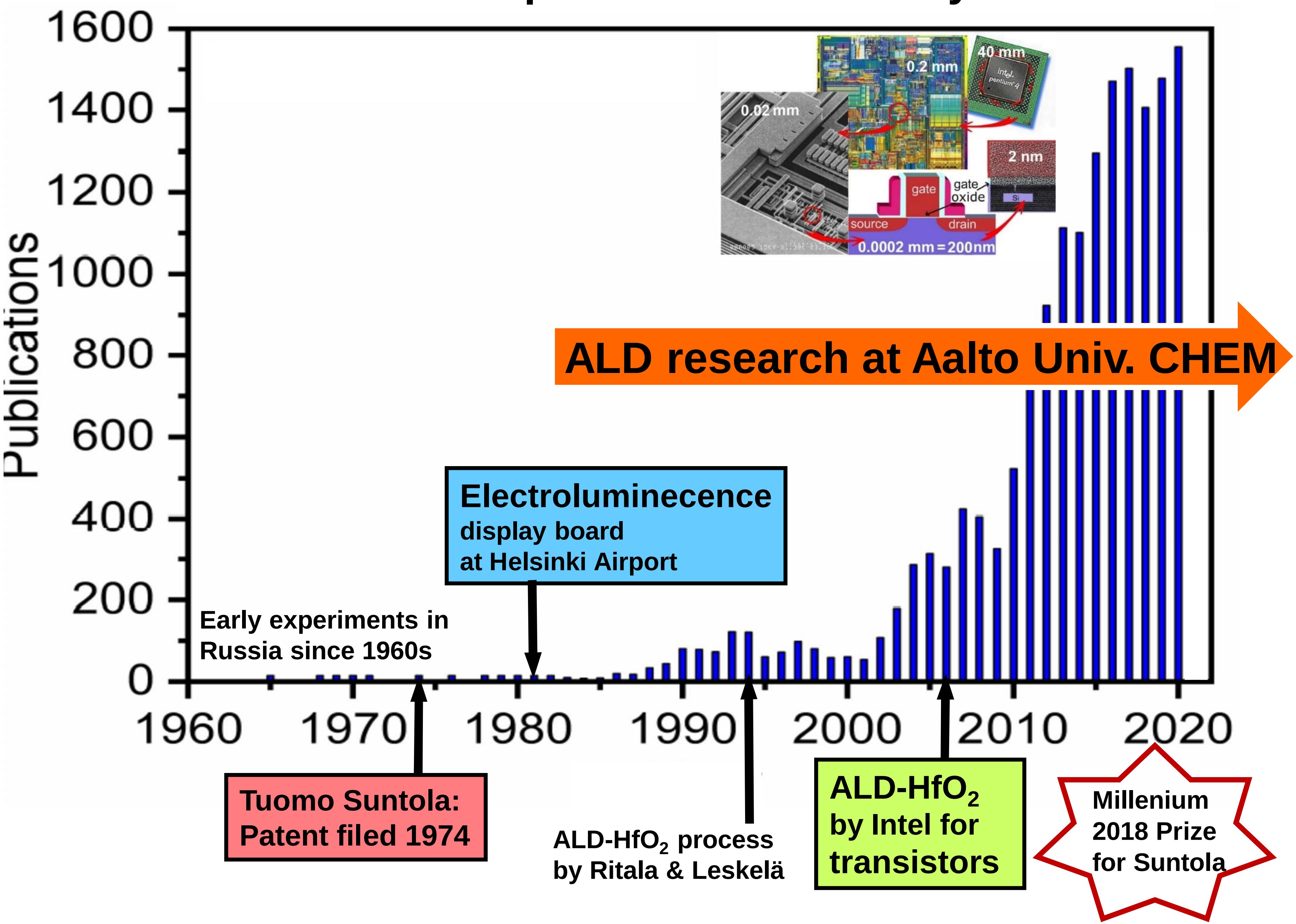
CMOS transistor

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

ALD: $HfCl_4$+H_2O

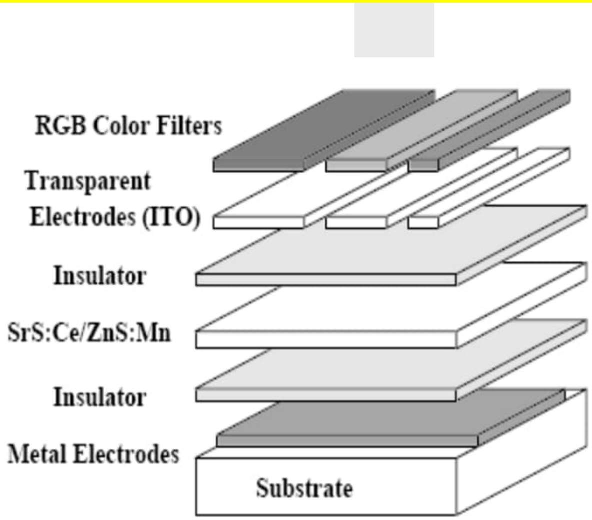


ALD publications annually



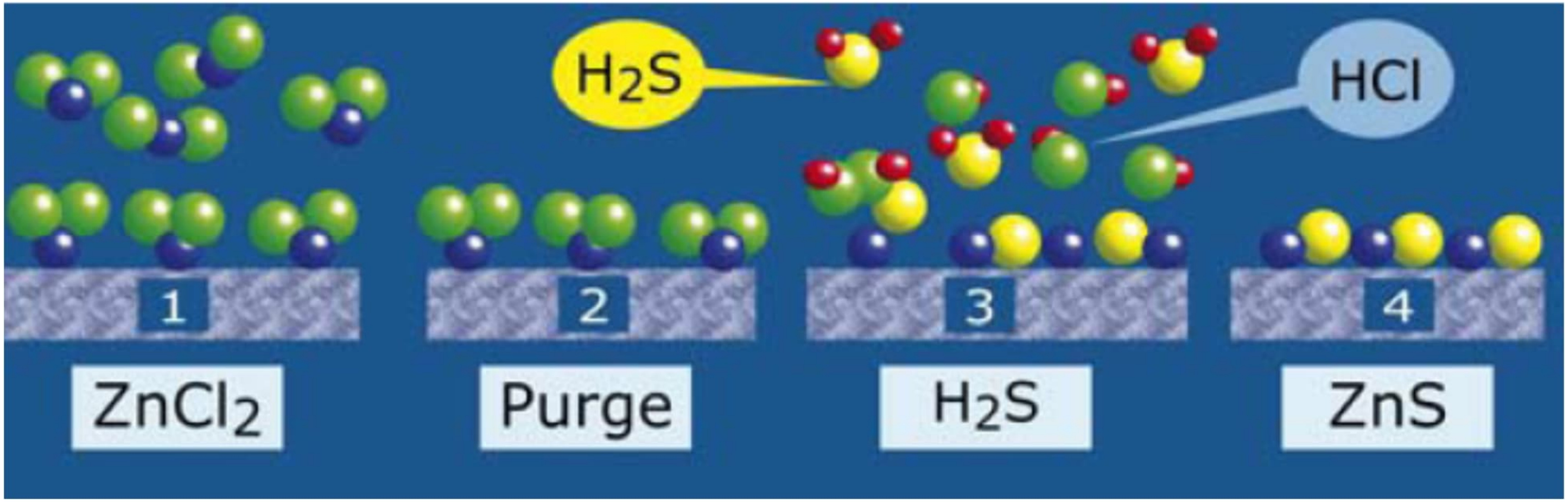
Atomic Layer Deposition (ALD) Thin-Film Technique

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



Electroluminescent display

Instrumentarium / Finlux / Planar

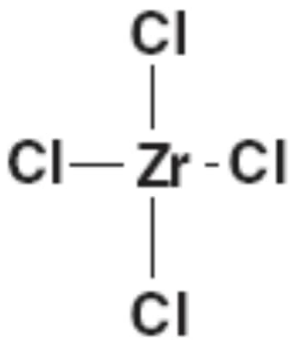


OXIDES (Al_2O_3, ZnO, TiO_2, ZrO_2 & HfO_2) &
ALD (atomic layer deposition) thin-film technology

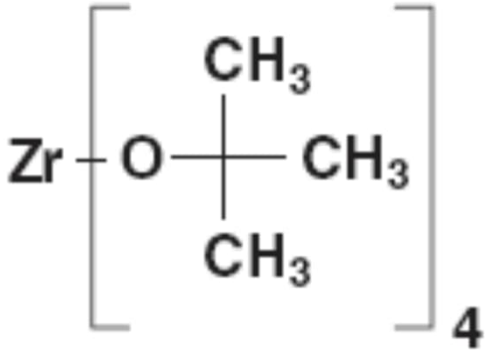
EXAMPLES of APPLICATIONS

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

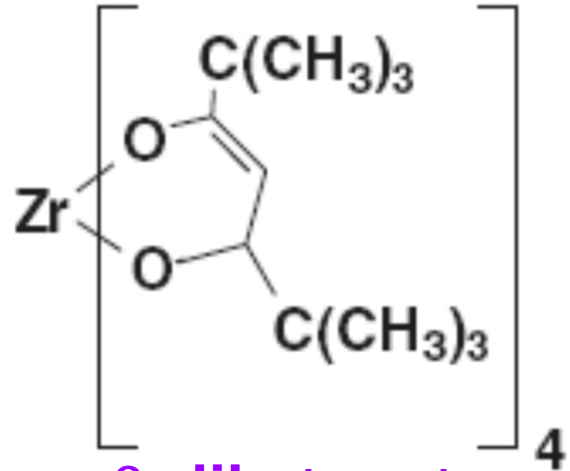
COMMON PRECURSORS in ALD



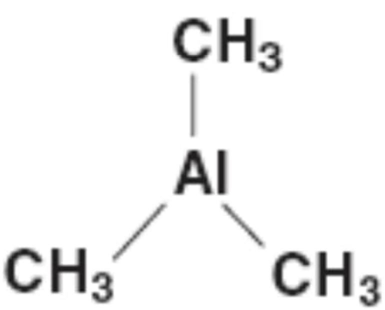
halides

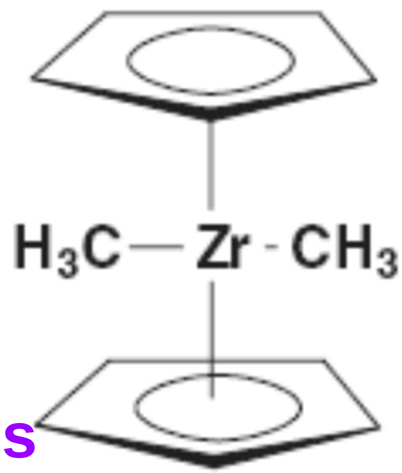


alkoxides

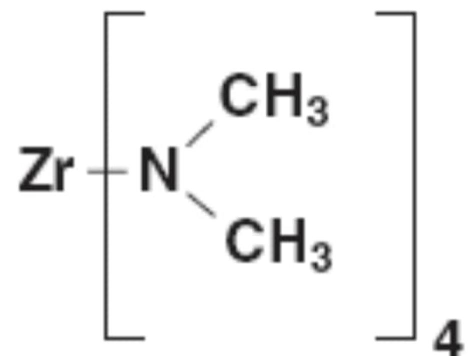


β-diketonates





organometallics



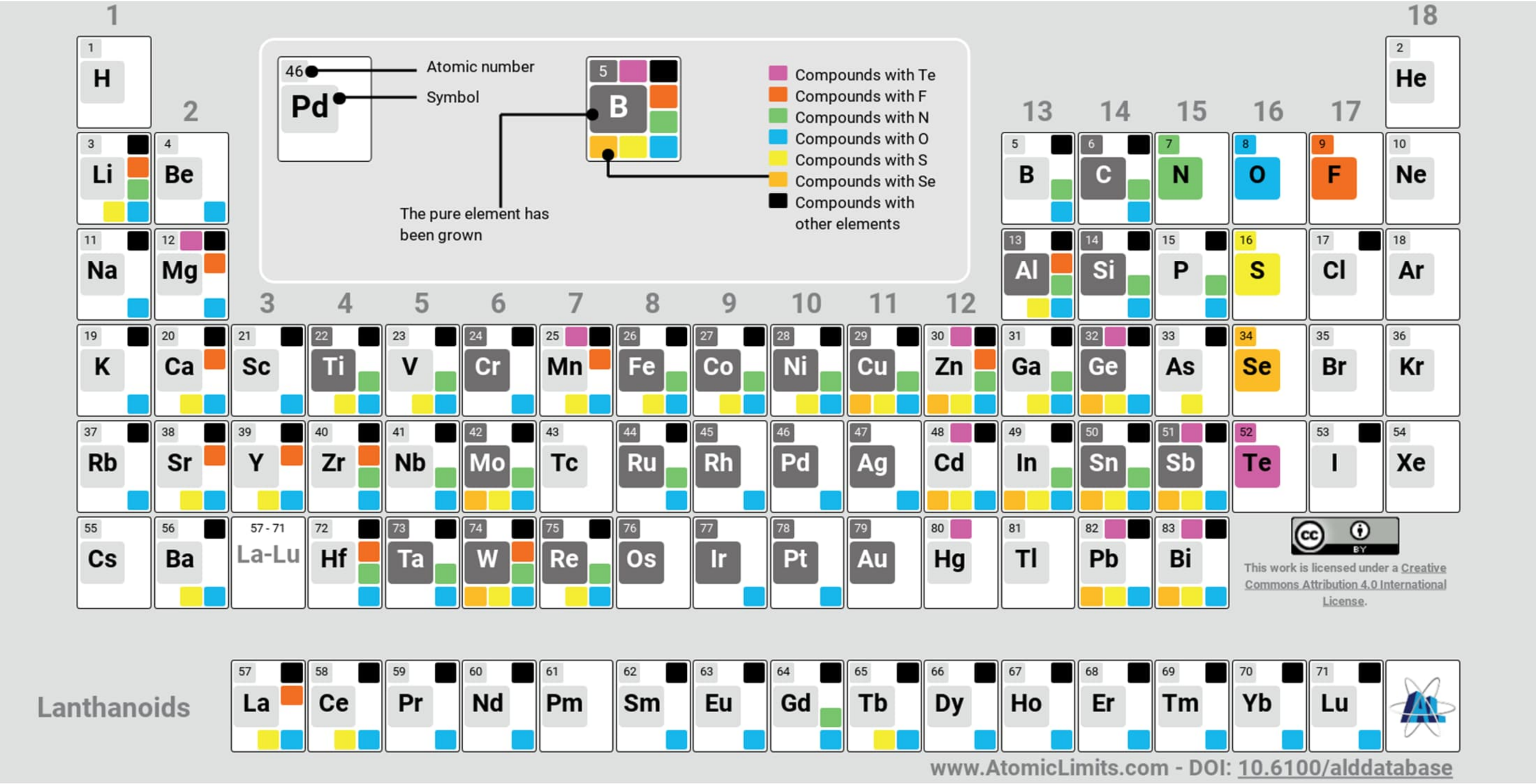
amido complexes

e.g. cyclopentadienyls

Common CO-REACTANTS (second precursor):

- **Water H_2O (e.g. with $TiCl_4$ 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

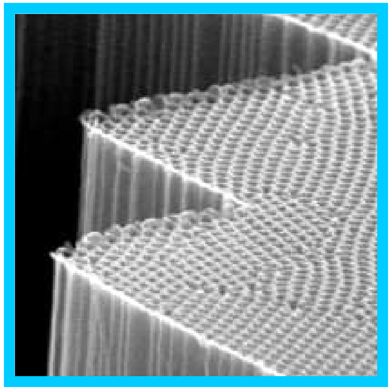
Advantages of ALD

ELECTRONICS

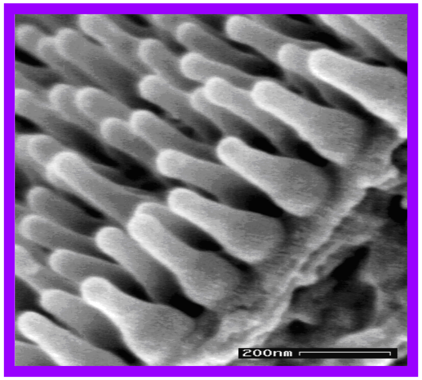
- Relatively inexpensive method
- Excellent repeatability
- Dense and pinhole-free films
- Accurate and simple thickness control
- Large area uniformity

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):

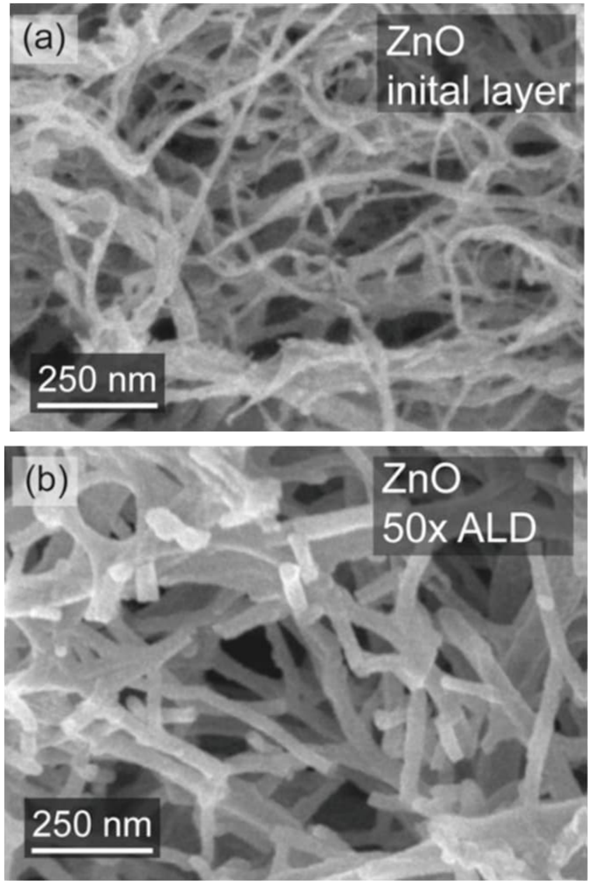
- **Al_2O_3 coating by ALD**

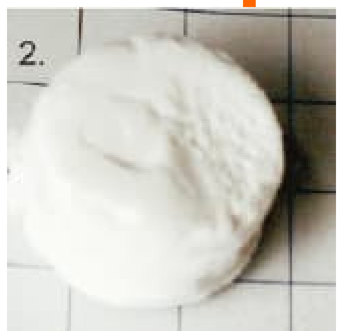
uncoated | **Al_2O_3-coated**

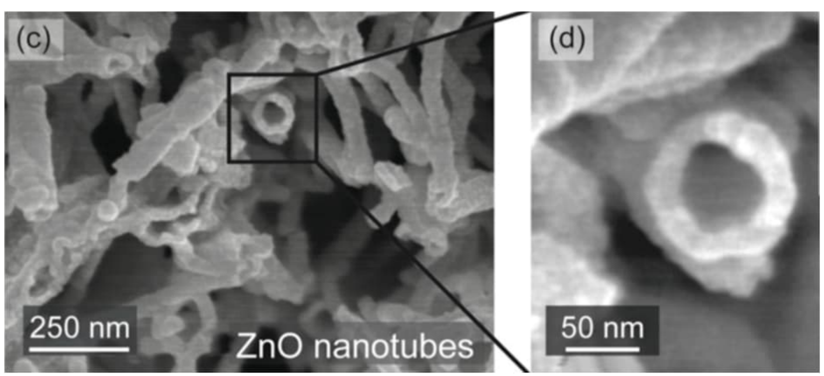
BEFORE | **AFTER TARNISHING TEST**

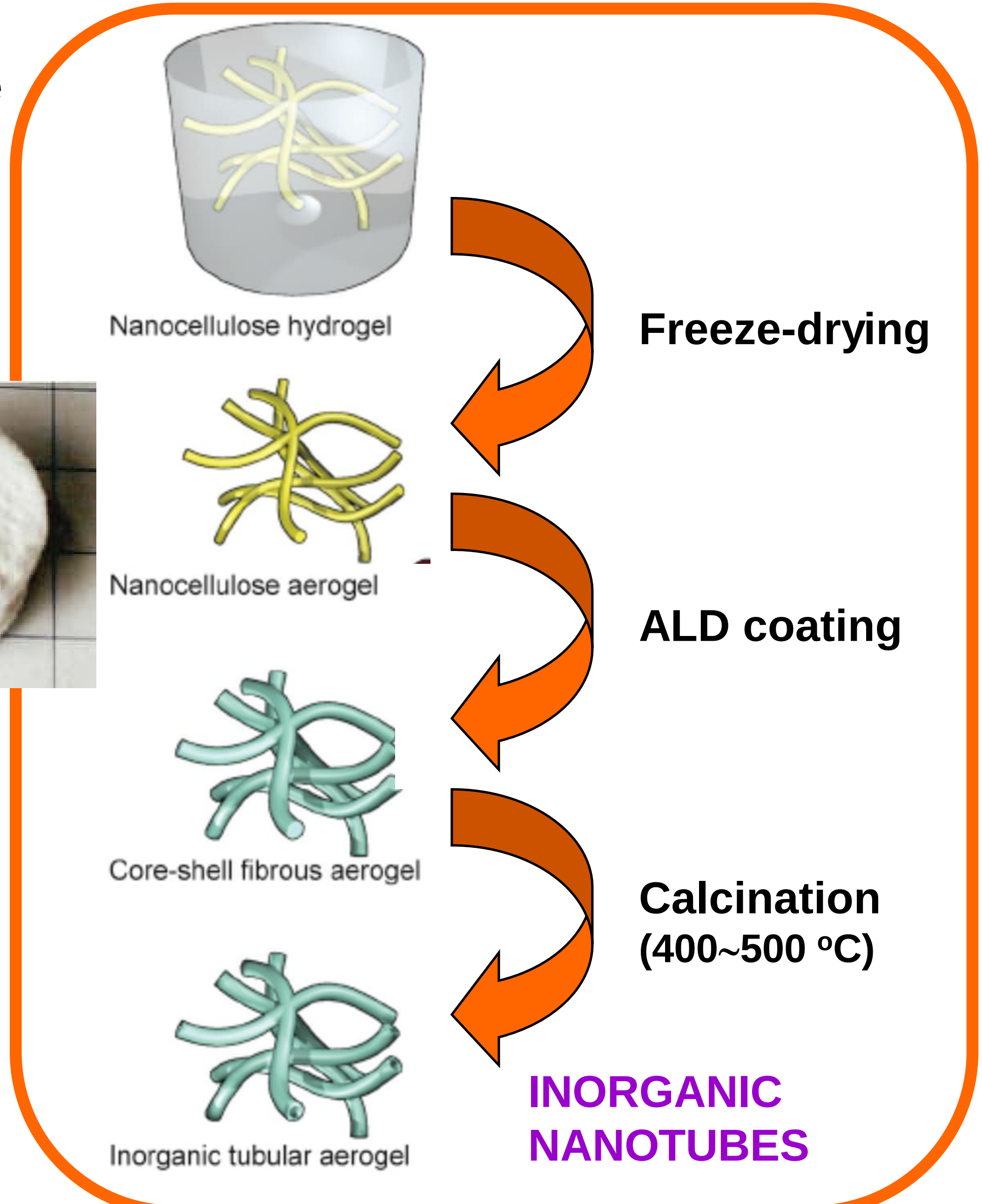
Dense, pinhole-free & highly conformal ALD-Al_2O_3-nanocoating efficiently protects silver jewelries from tarnishing

NANOSTRUCTURING by ALD
- nanocellulose aerogel template

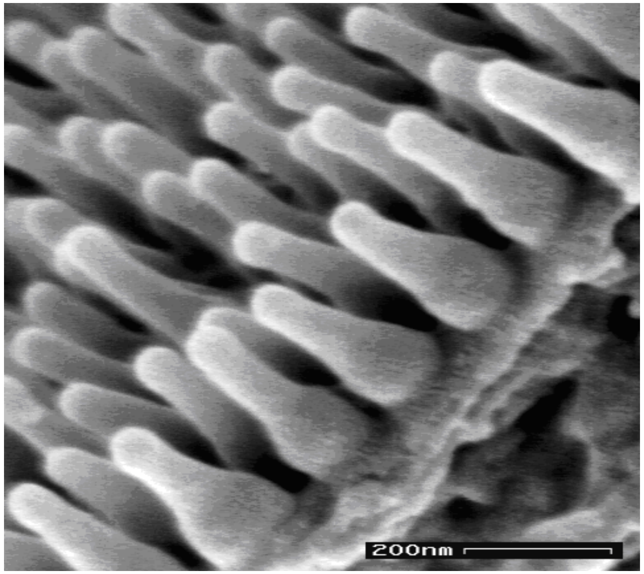








J.T. Korhonen, J. Malm, M. Karppinen,
O. Ikkala & R.H.A. Ras, *ACS Nano* 5, 1967 (2011).



CICADA WING

- Peculiar surface-nanostructure

  200-nm high nanopillars coated with a waxy layer

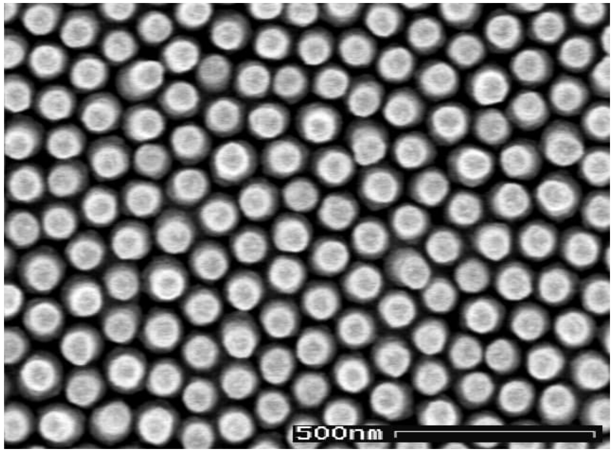
- superhydrofobic

ZnO

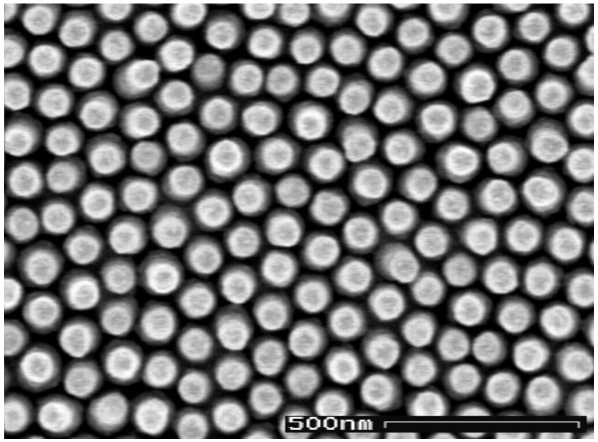
- Reversible change from hydrofobic to hydrophilic upon UV-radiation

CICADA WING + ZnO

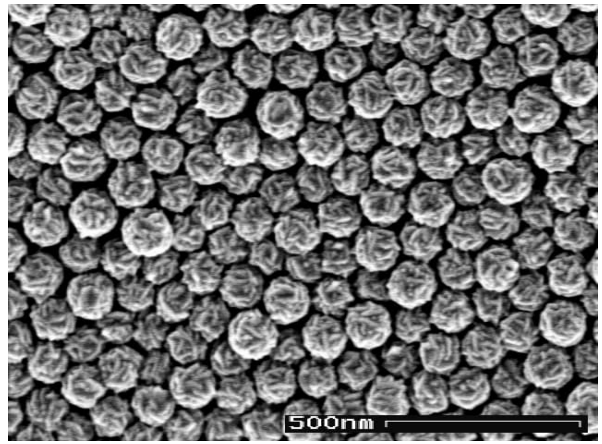
- Conformal coating of the wing by a thin layer of ZnO (~20 nm) by means of ALD
- Reversible change from superhydrofobic to superhydrophilic upon UV-radiation



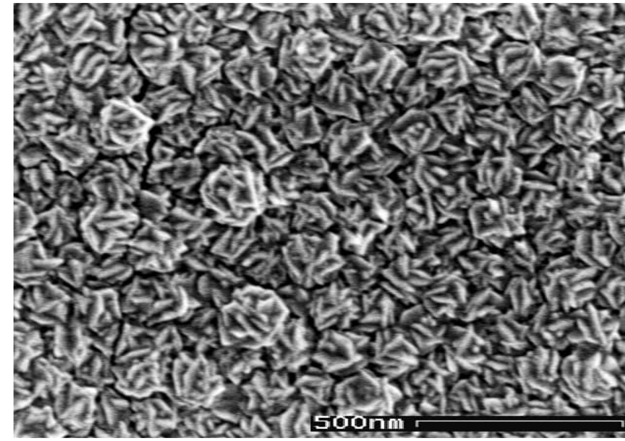
J. Malm, E. Sahramo, M. Karppinen & R. Ras, *Chem. Mater.* **22**, 3349 (2010).



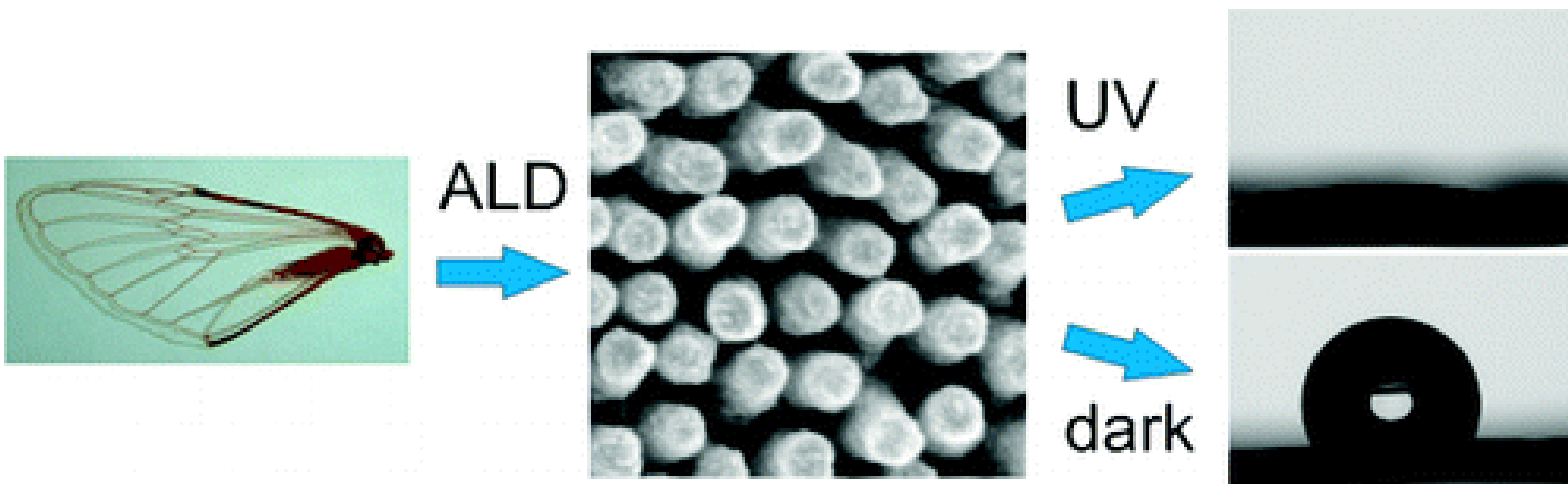
100 cycles (20 nm)

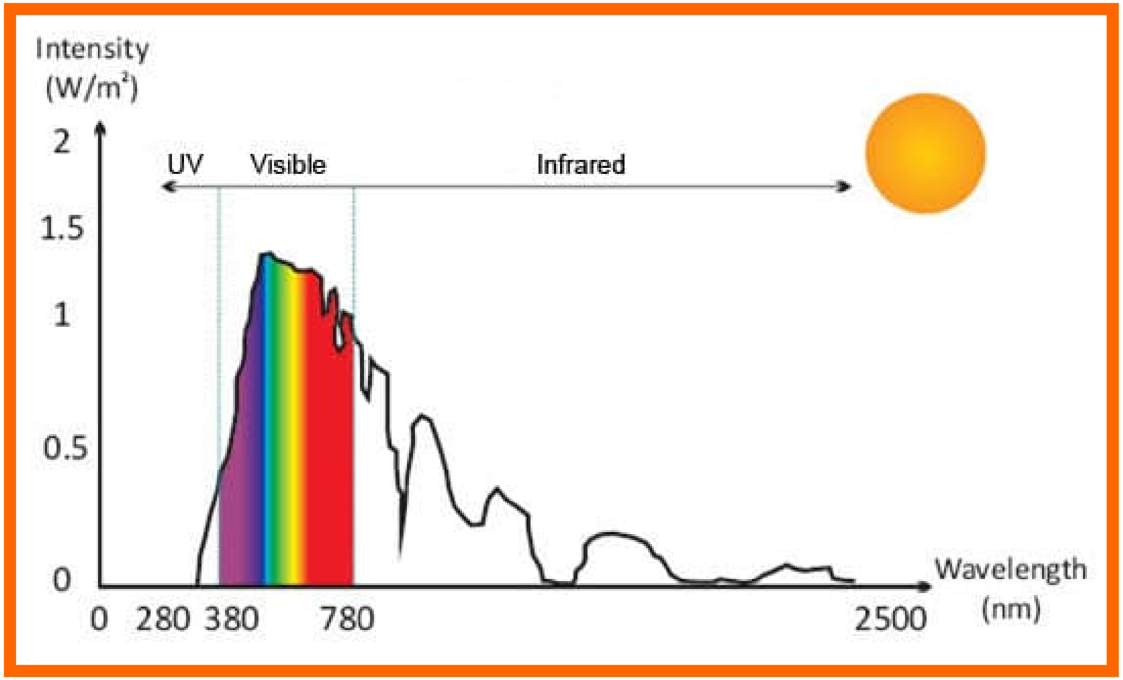


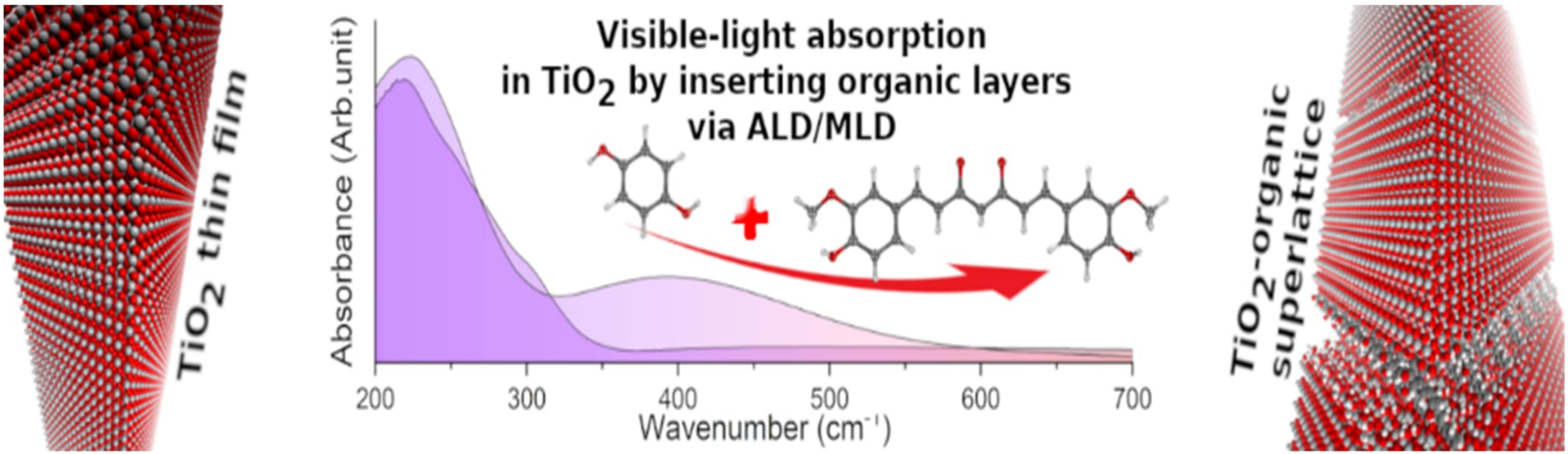
300 cycles (60 nm)



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).