TENTATIVE LECTURE SCHEDULE

		Date	Topic
1.	Mon	13.09.	Course Introduction & Short Review of the Elements
2.	Wed	15.09.	Periodic Properties & Periodic Table & Main Group Elements (starts)
3.	Fri	17.09.	Short Survey of the Chemistry of Main Group Elements (continues)
4.	Mon	20.09.	Zn + Ti, Zr, Hf & Atomic Layer Deposition (ALD)
5.	Wed	22.09.	Transition Metals: General Aspects & Pigments
6.	Mon	27.09.	Ag, Au, Pt, Pd & Catalysis (Antti Karttunen)
7.	Wed	29.09.	Redox Chemistry
8.	Mon	04.10.	Crystal Field Theory
9.	Wed	06.10.	V, Nb, Ta & Metal Complexes & MOFs
10.	Fri	08.10.	Cr, Mo, W & 2D materials
11.	Mon	11.10.	Mn, Fe, Co, Ni, Cu & Magnetism & Superconductivity
12.	Wed	13.10.	EXTRA
13.	Fri	15.10.	Resources of Elements & Rare/Critical Elements & Element Substitutions
14.	Mon	18.10.	Lanthanoids + Actinoids & Luminescence (Down/Upconversion)
15.	Wed	20.10.	Inorganic Materials Chemistry Research

EXAM: Thu Oct. 28, 2021

PRESENTATION TOPICS/SCHEDULE

Wed	06.10.	Nb:	
Fri	08.10.	Mo:	Ahmed, Shamshad
Mon	11.10.	Mn:	Majaniemi, Thakur
		Ru:	
Wed	13.10.	Co:	Ekholm, Olander, Syväniemi
		Cu:	Kolawole, Nguyen, Munib
Fri	15.10.	In:	Kovanen, Ogunyemi
		Te:	Huhtakangas, Wallin, Kaarne
Mon	18.10.	Eu:	Sonphasit, Ichanson, Tuisku
		Nd:	Jussila, Siuro, Perttu
		U:	Sinkkonen, Wennberg, Partanen

QUESTIONS: Lecture 4

1. 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?

2. 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.

3. ZnO is a wide bandgap semiconductor and promising material for many (opto)electrical applications.

   (a) To enhance its n-type electrical conductivity through chemical substitution (= doping), which element has been used as a substituent?

   (b) Nobody has so far been able to realize p-type conducting ZnO, even though ths would be useful for some applications. If you would like to challenge this goal, which element you would select for the substituent? Explain why?

4. Which element is commonly used as a substituent to create oxygen vacancies in ZrO_2 ? Why ?

5. Why in ALD technique:

   (a) Film thickness control is straightforward?

   (b) Conformal coating is readily achieved?

Group → ↓Period	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1 H																	2 He
2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba	*	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra	**	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Uut	114 Fl	115 Uup	116 Lv	117 Uus	118 Uuo
		*	57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu	
		**	89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr	

Al	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^1$
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	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^6\ 5s^2\ 4d^{10}\ 5p^6\ 6s^2\ 4f^{14}\ 5d^2$

Al^{3+}	$1s^2\ 2s^2\ 2p^6$
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+}	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^6\ 5s^2\ 4d^{10}\ 5p^6\ 4f^{14}$

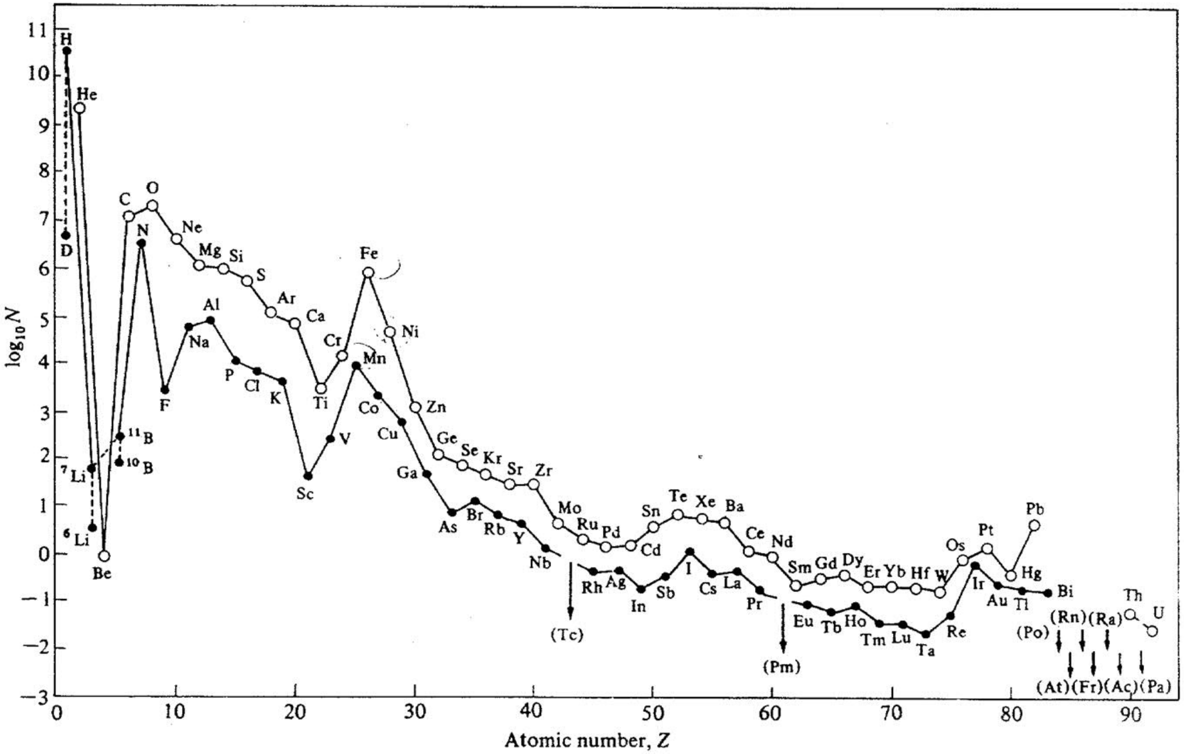
IONIC RADII (in Å)

		Ti	Zr	Hf	Zn	Al
+2	CN-4	-	-	-	0.60	-
	CN-5	-	-	-	0.68	-
	CN-6	0.86	-	-	0.74	-
	CN-8	-	-	-	0.90	-
+3	CN-4	-	-	-	-	0.39
	CN-5	-	-	-	-	0.48
	CN-6	0.67	-	-	-	0.54
+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)**

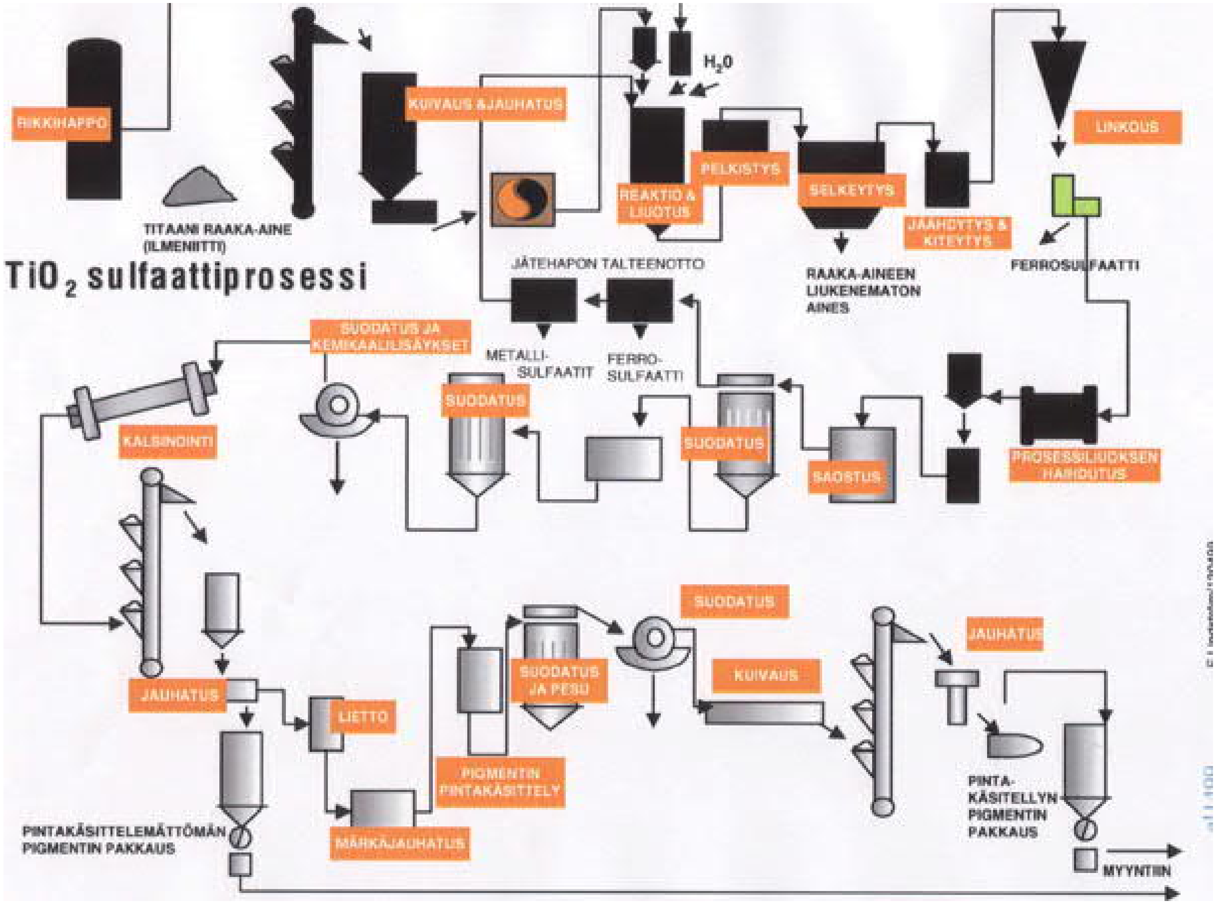
TiO_2:n valmistus

Sulfaattiprosessi: Pori

Raaka-aine (ilmeniitti) liuotetaan rikkihappoon ja syntyvästä liuoksesta titaani saostetaan titaanihydraattina. Hydraatti pestään, kalsinoidaan ja pintakäsitellään. Prosessi kestää 2 viikkoa.

Kloridiprosessi:

Raaka-aine (rutiili) kloorataan, jolloin muodostuu titaanitetrakloridia. Tetrakloridi hapetetaan (hapella) kaasufaasissa titaanidioksidiksi ja pintakäsitellään kuten sulfaattiprosessissakin. Kloridiprosessilla valmistetaan vain rutiilirakenteen omaavaa titaanidioksidia.

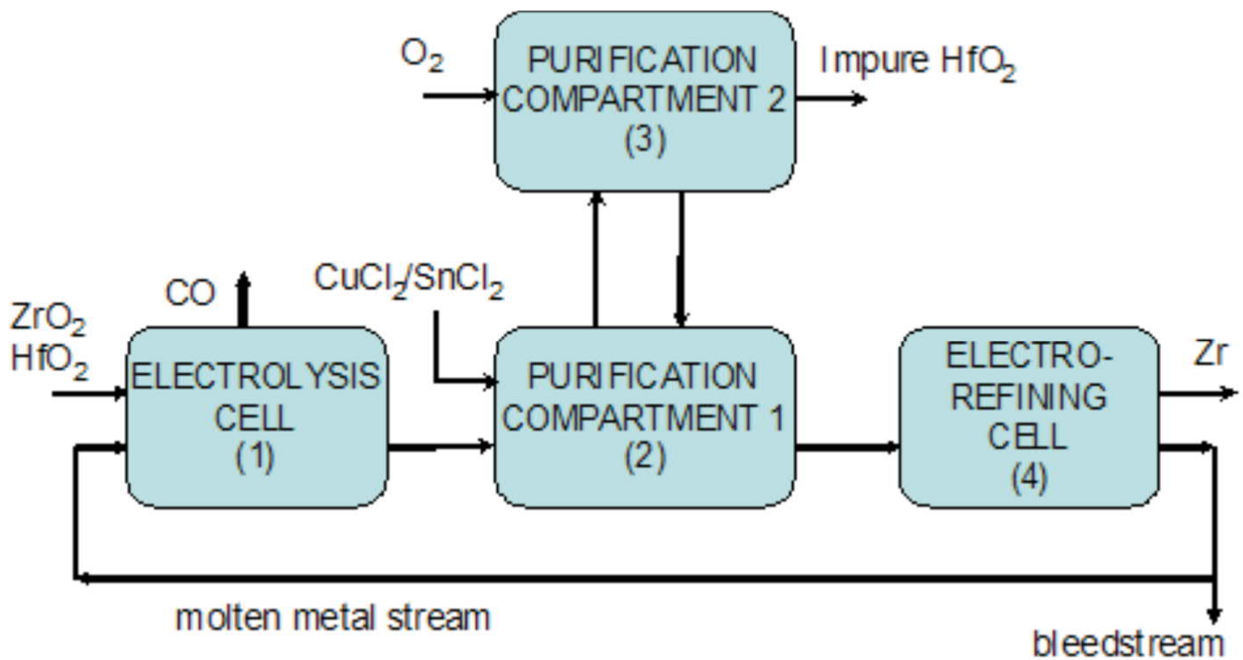


Zr & Hf

- **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

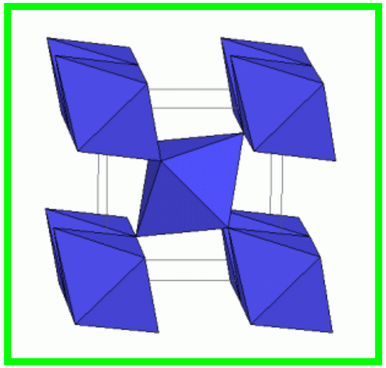
- **Zr:** very low neutron absorption → used to make containers for nuclear fuel
- **Hf:** very high neutron absorption → used in control rods
- For the use of Zr in nuclear fuel containers it is crucial to ensure that the Zr metal used has extremely low Hf content
- Several techniques for the separation developed, below shown is a new advanced technique developed at University of Ghent

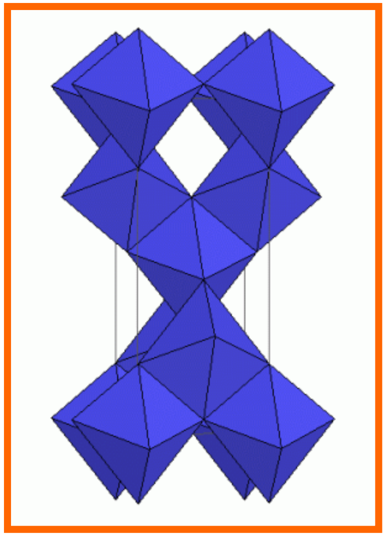


Role of Zinc in the structure and function of proteins

- Required for essential 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} and thus **no crystal field effect**: environment around Zn^{2+} is flexible to allow for the precise adjustment to the surroundings without an energy penalty

TiO_2 (important chemical produced worldwide)

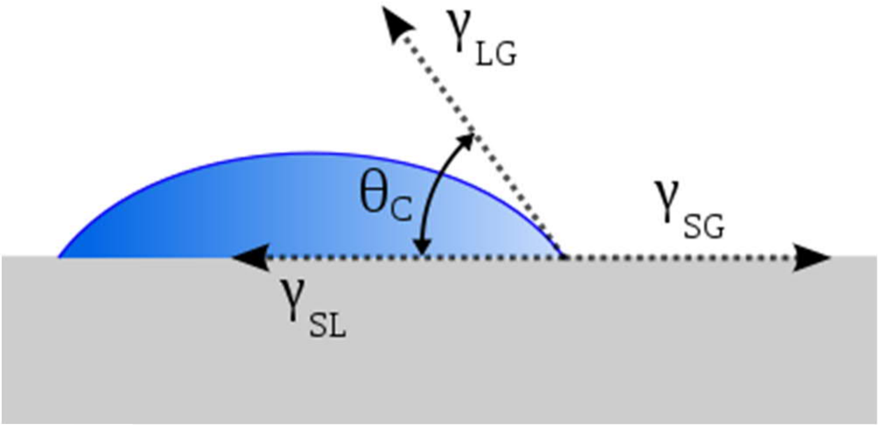


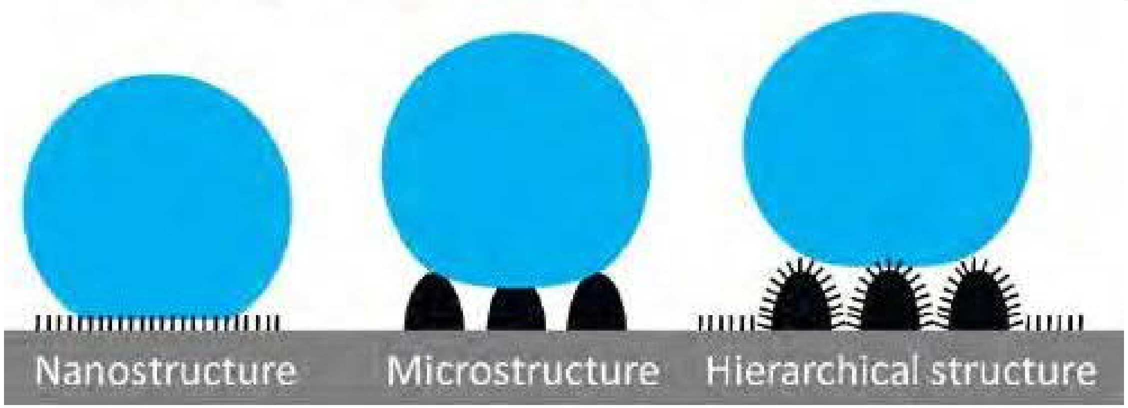


- **Crystal structures:** - rutile, anatase, brokite
- **White pigment:**
  - large refractive index
  - used in paints, paper, plastics, cosmetics, foods, tooth pastes, …
- **UV protection:** - sunscreens, plastics
- **Inert:** - filler material in pharmaceuticals
- **Photocatalytic:**
  - Akira Fujishima 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

SUPERHYDROPHOBICITY

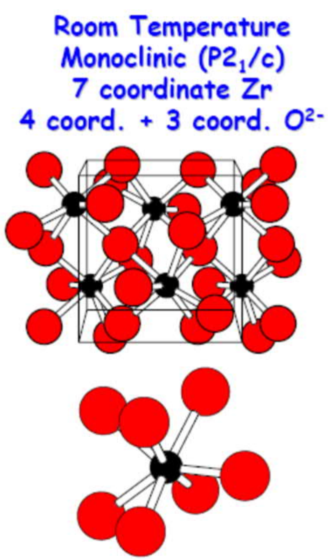
- Water forms perfect droplets on surface
  → surface extremely difficult to wet
  → Lotus effect
- Contact angle (θ_C):
  angle for liquid droplet at three-phase (liquid-gas-solid) boundary
- SUPERHYDROPHOBICITY:
  contact angle > 150°

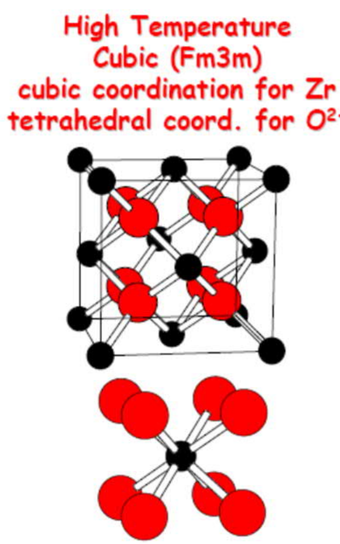


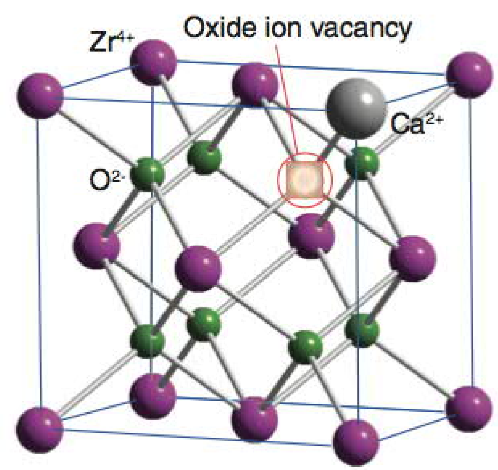


ZrO_2

- Used as industrial ceramics, protective coating (e.g. on TiO_2 pigment particles) and refractory material in e.g. insulation
- 7-coordinated (monoclinic) structure at RT &
  8-coordinated cubic structure at high temperatures
- Y^{III}-forZr^{IV} substitution stabilizes the cubic ZrO_2 structure synthesized in various colours (gemstone & diamond simulant)
- 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)

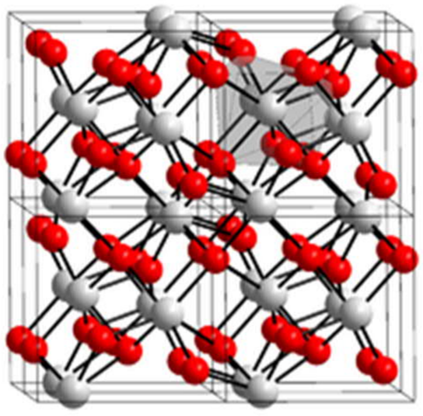






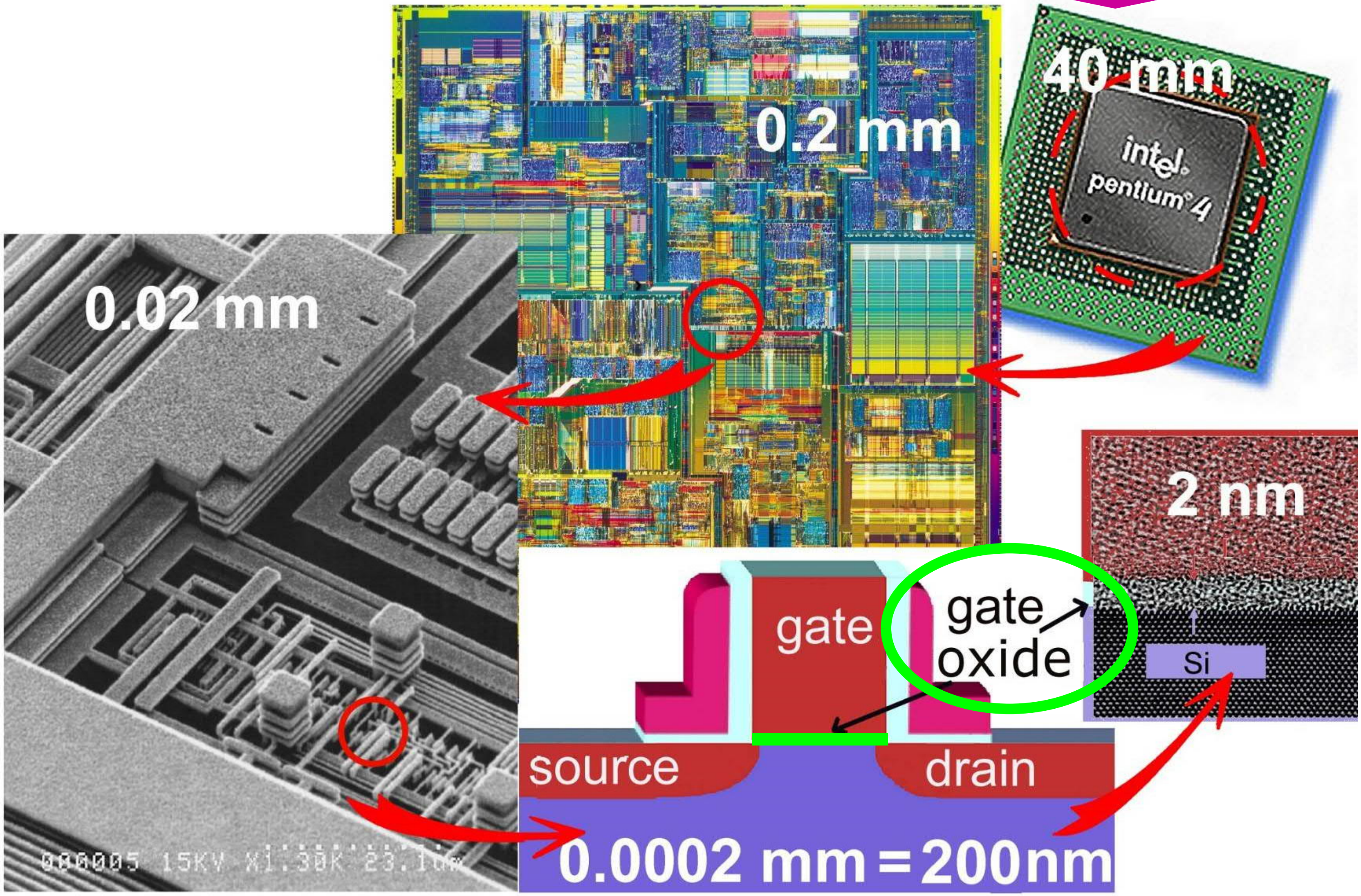
HfO_2

- Similar (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



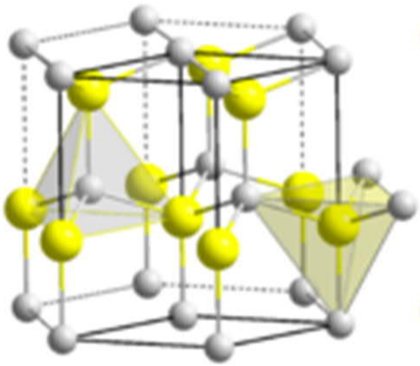
CMOS transistor

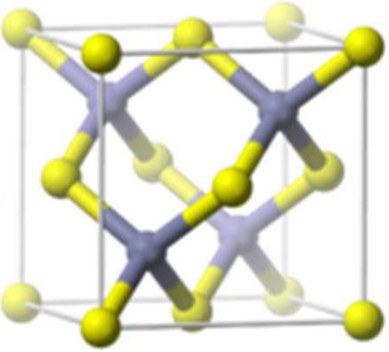
smaller transistors → lower gate voltage
same electric fields → thinner dielectric
SiO_2 → **HIGH-*k* DIELECTRICS**



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





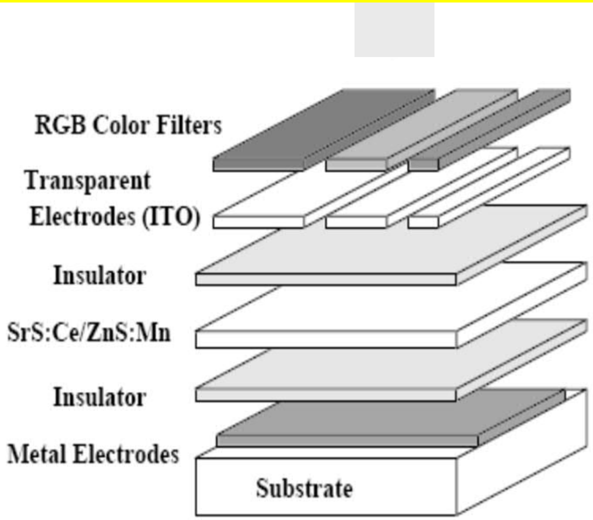
OXIDES (Al_2O_3, ZnO, TiO_2, ZrO_2 & HfO_2) & ALD (atomic layer deposition) thin-film technology

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
- ALD-Al_2O_3 (amorphous): barrier and protective coating

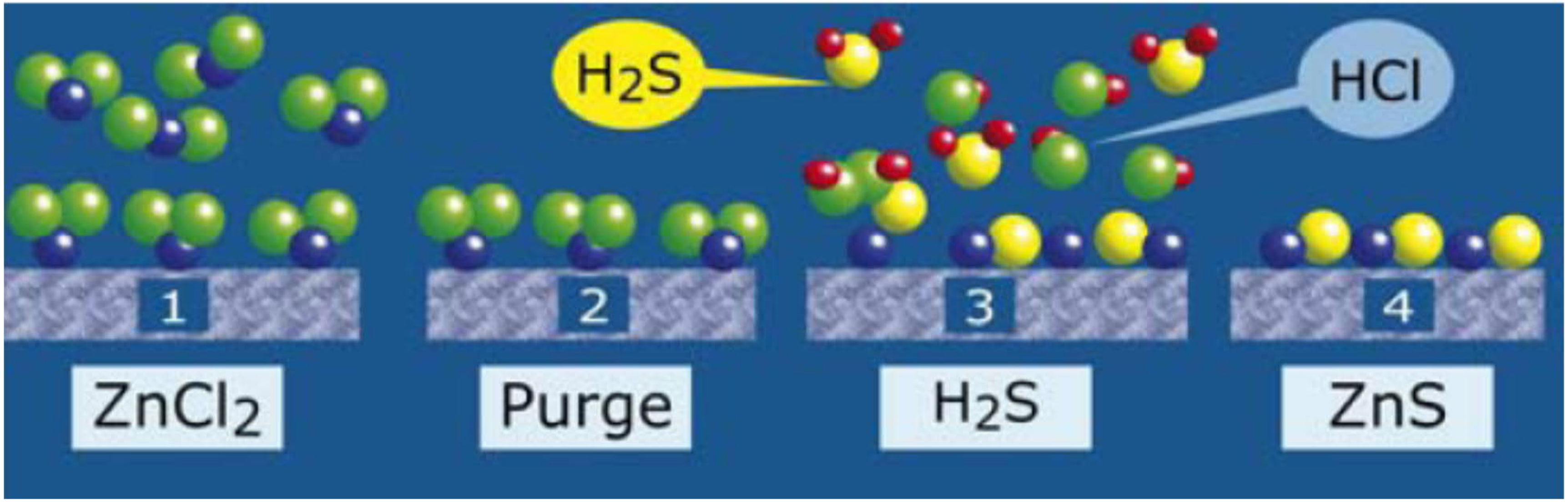
Atomic Layer Deposition (ALD) Thin-Film Technique

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

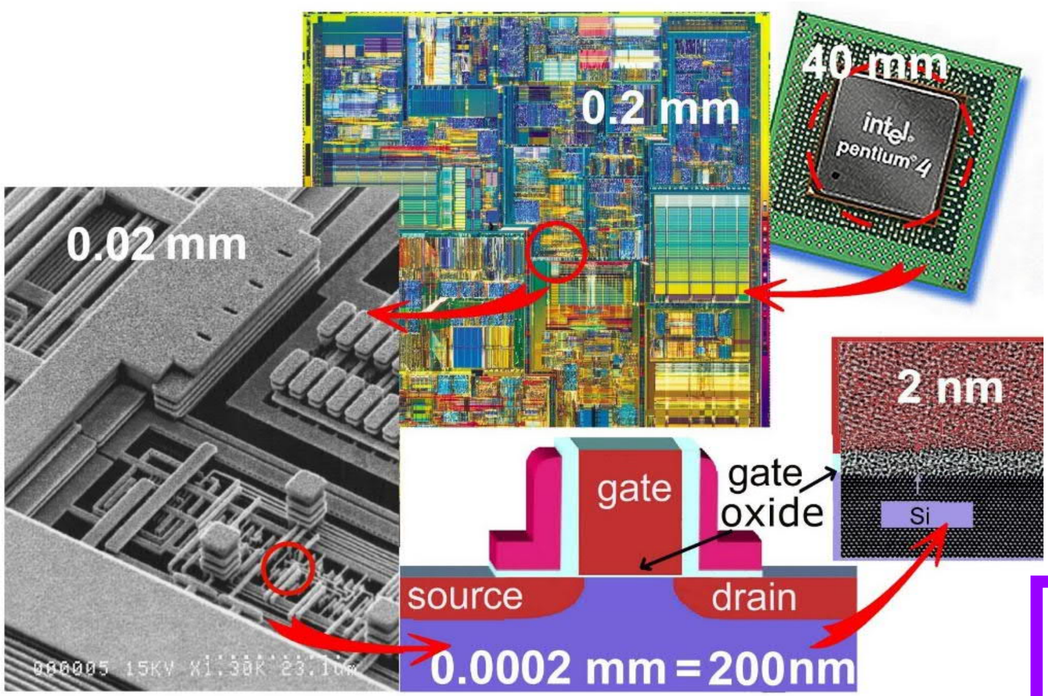


Electroluminescent display

Instrumentarium / Finlux / Planar



Atomic Layer Deposition (ALD) Technology

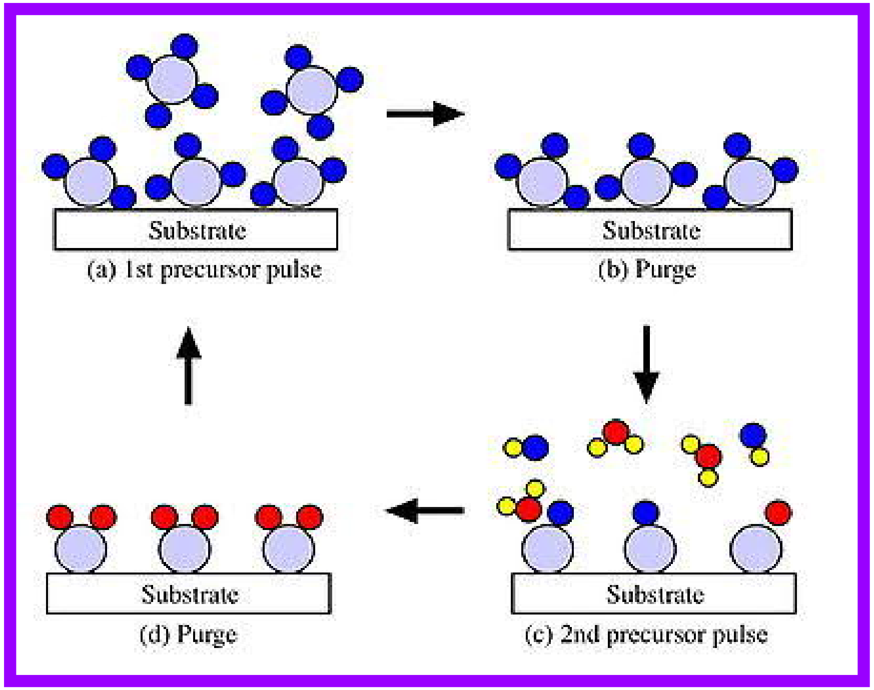


- High-quality (pinhole-free)
- Thickness control (atomic level)
- Large-area homogeneity
- Conformity → Nanostructuring

CMOS transistor

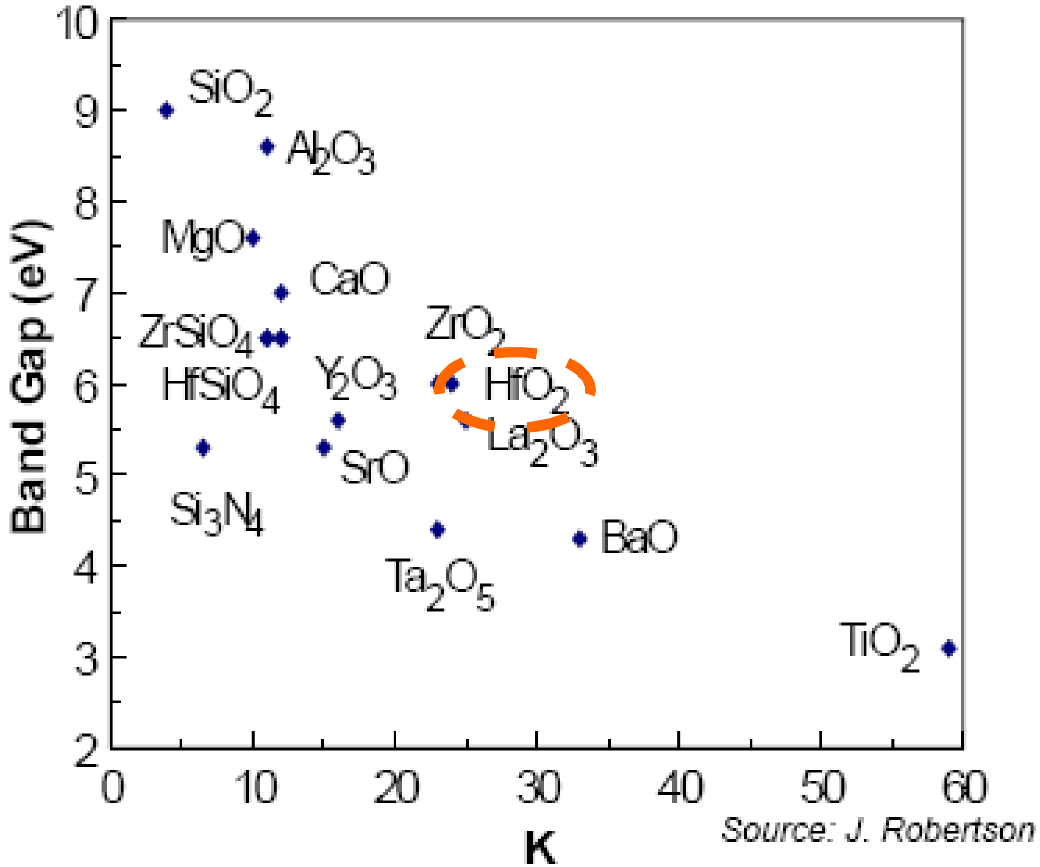
- 2-nm amorphous HfO_2 gate-oxide layer deposited by ALD

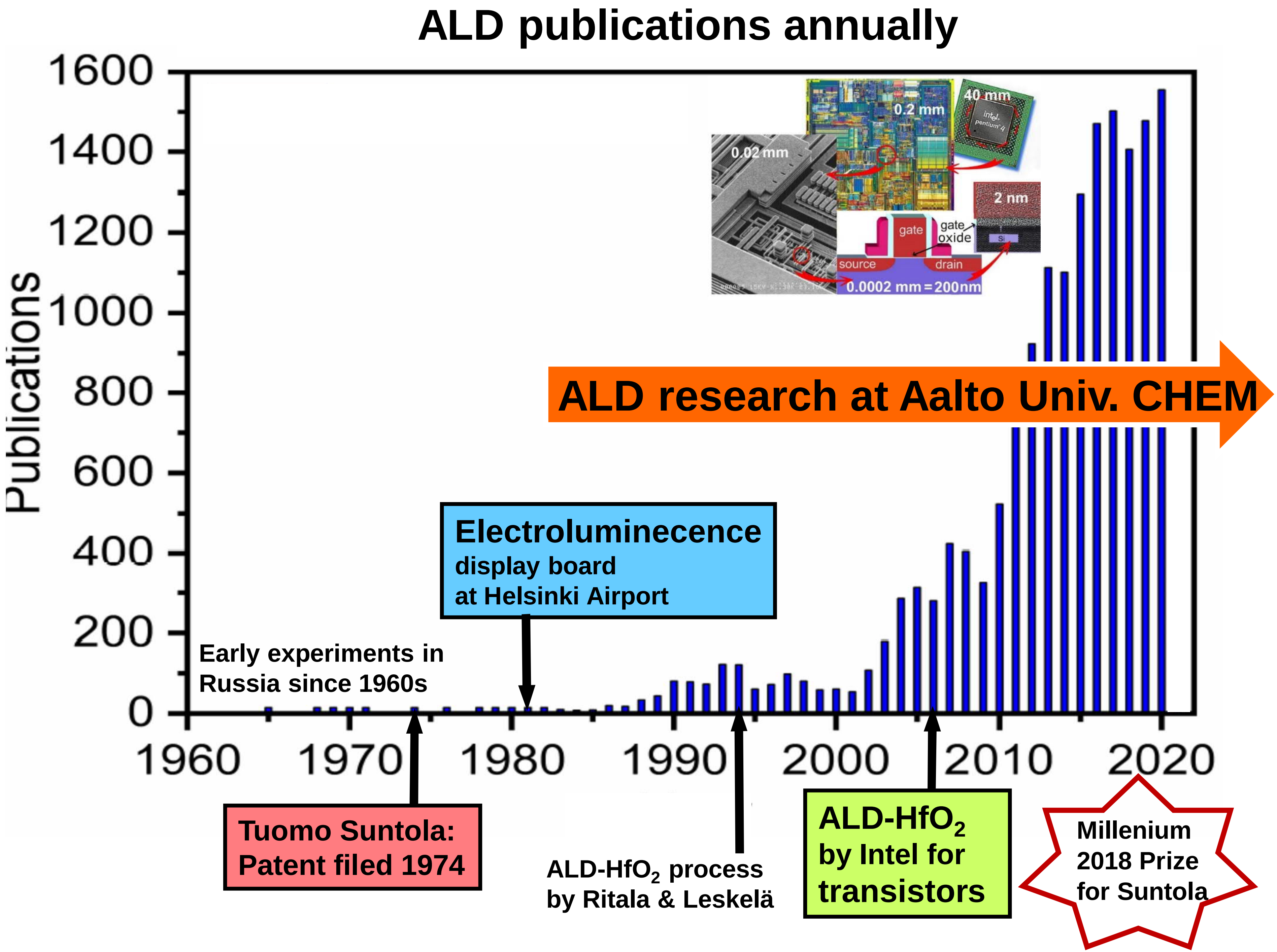
ALD: $HfCl_4$+H_2O



Conditions for high-*k* dielectrics

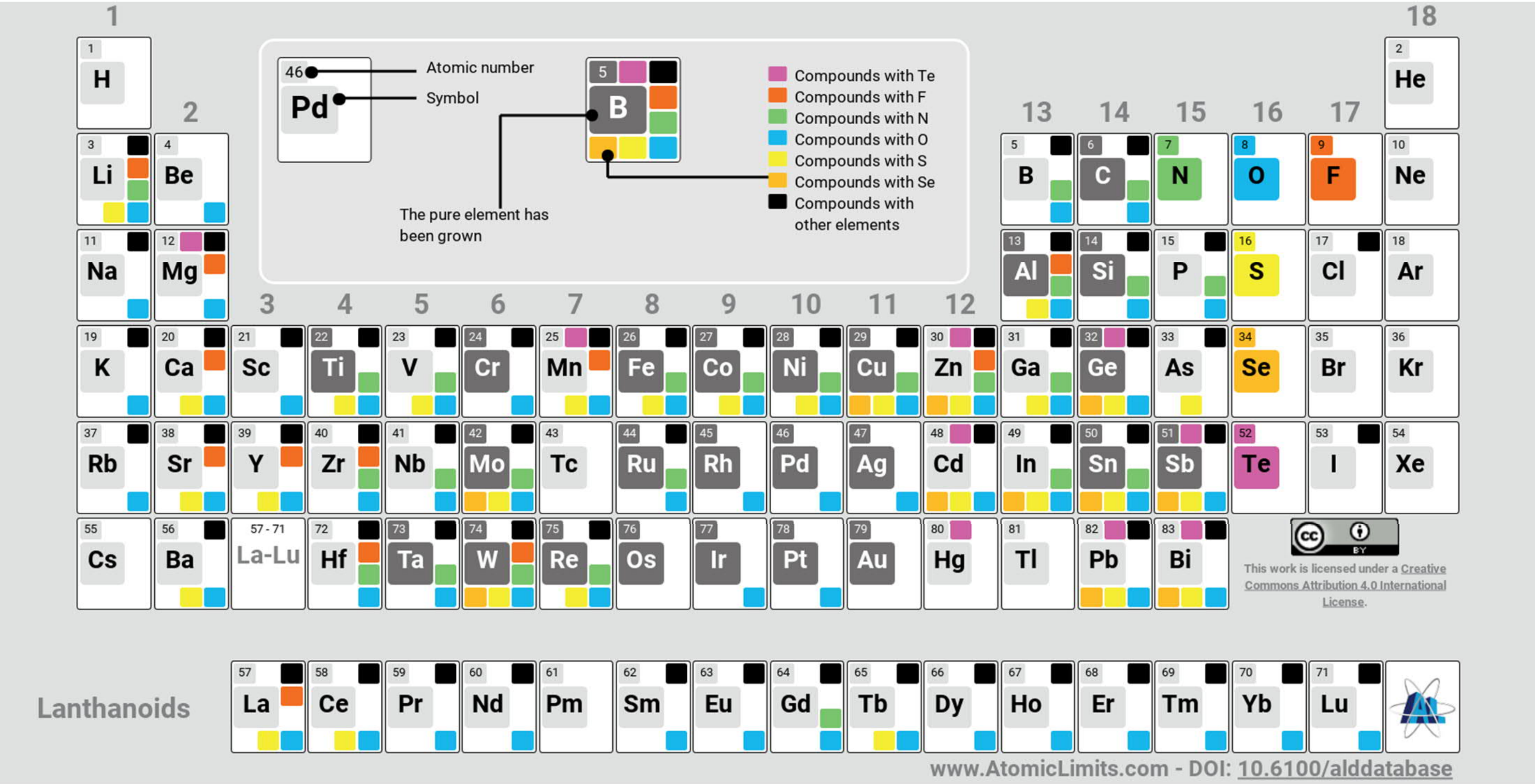
- High enough **dielectric constant *k***
- Wide **band gap** for low leakage
- Stable – no reaction with Si
- Good interface, low impurities





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

Periodic Table of ALD Processes



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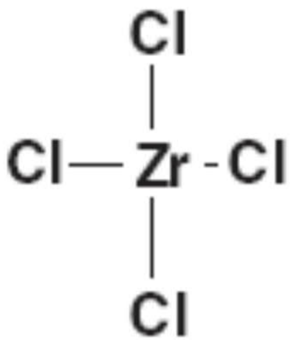
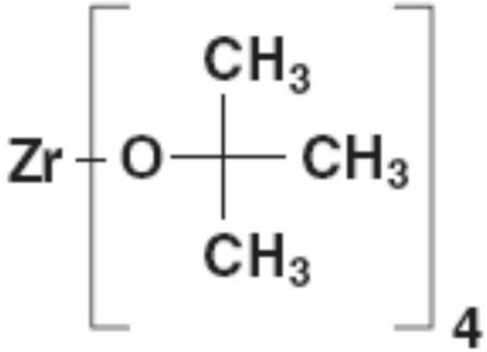
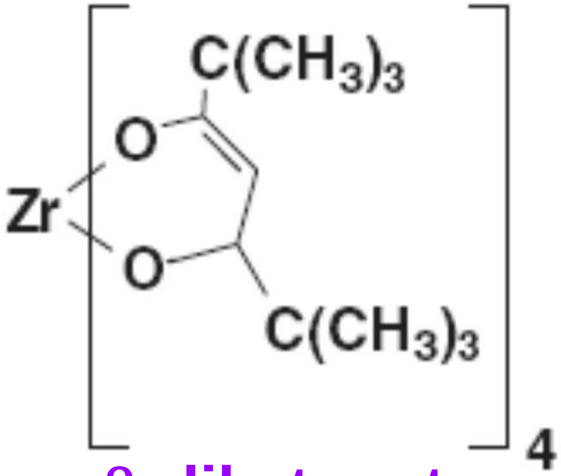
COMMON PRECURSORS in ALD



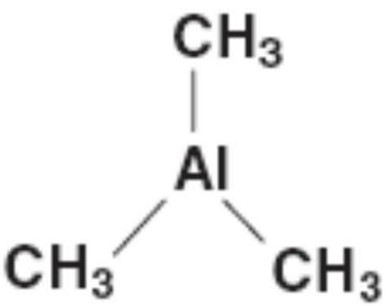
halides

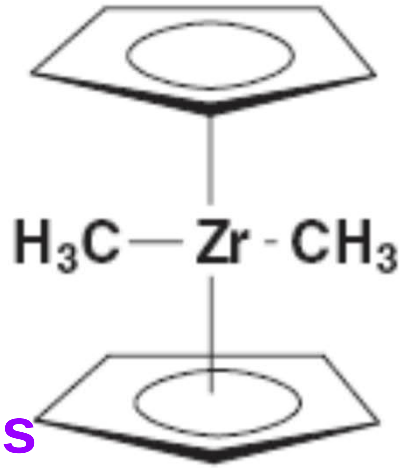


alkoxides

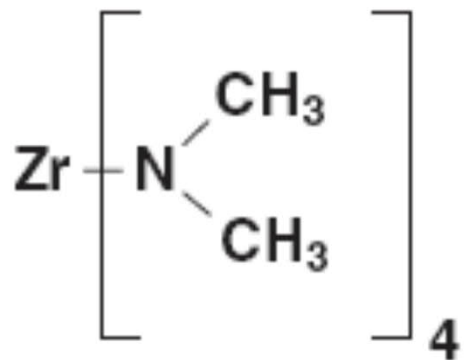


β-diketonates





organometallics



amido complexes

e.g. cyclopentadienyls

Most Common ALD METALS: Al, Zn, Ti, Hf

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**

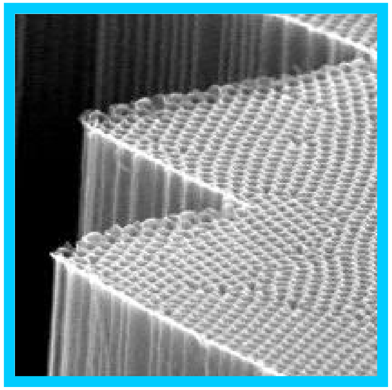
Advantages of ALD

ELECTRONICS

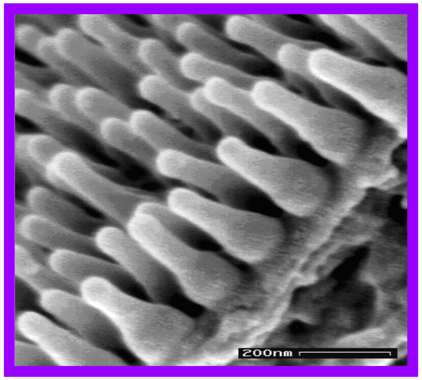
- Relatively inexpensive method
- Excellent repeatability
- Dense and pinhole-free films
- Accurate and simple thickness control
- Large area uniformity

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**

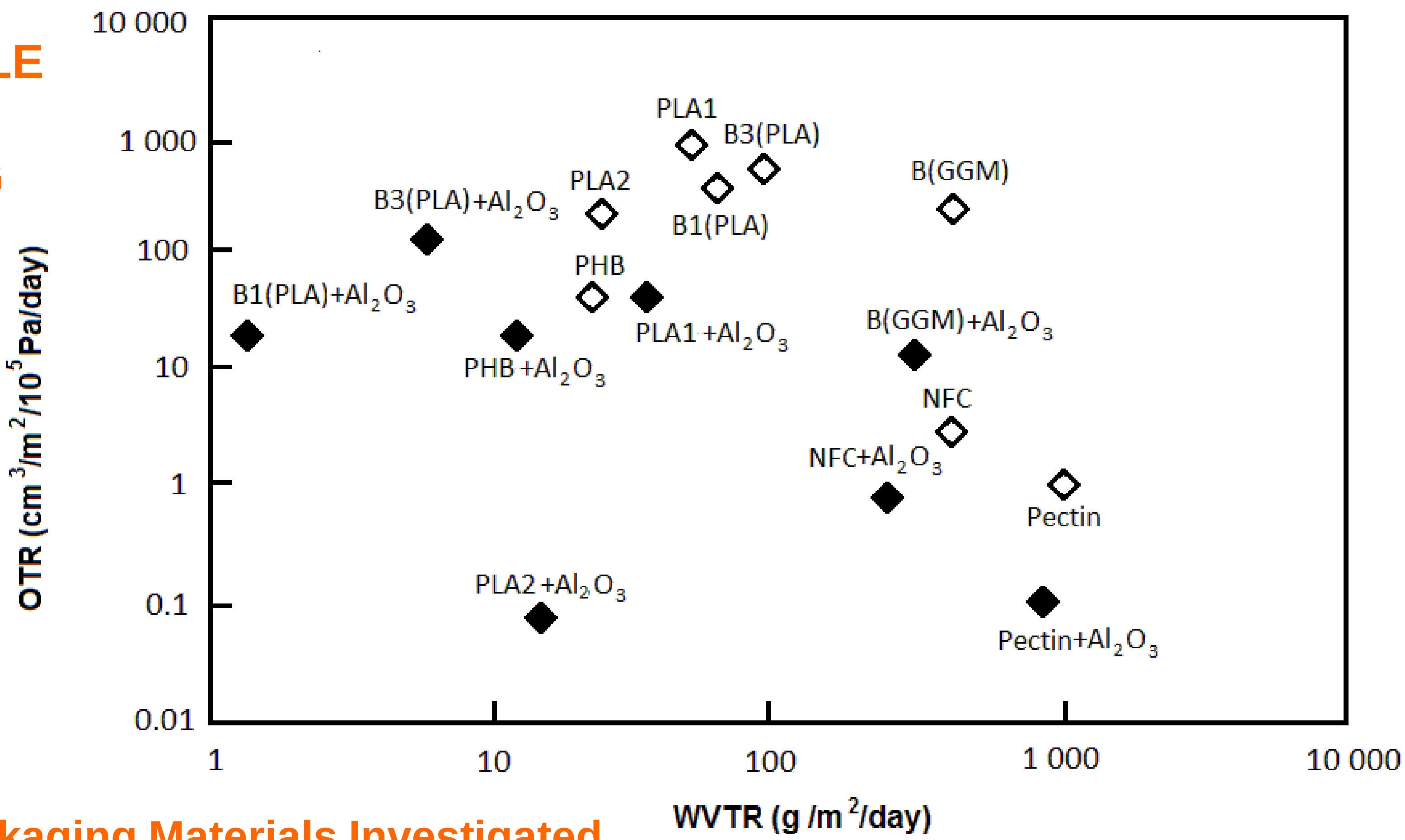
	uncoated	**Al_2O_3-coated**

BEFORE **AFTER TARNISHING TEST**

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

RECYCLABLE BIO-BASED PACKAGING MATERIALS

Problem: Bad gas-barriers



Bio-based Packaging Materials Investigated

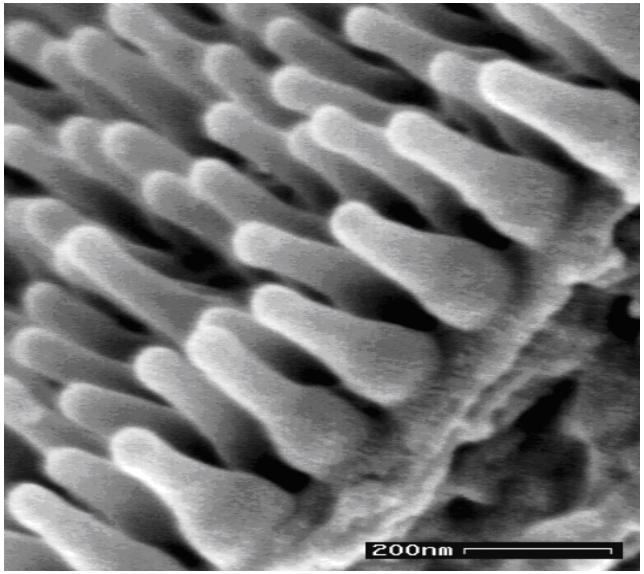
B(PLA)	**Polylactide-coated board**
PLA	**Polylactide film**
NFC	**Nano-fibrillated cellulose film**
B(GGM)	**Galactoclugomannan-coated board**
PHB	**Polyhydroxy butyrate film**
Pectin	**Pectin film made by solution casting**

O_2- and H_2O-vapour transmission

◇ **Biopolymer**

◆ **Biopolymer + 25 nm ALD-Al_2O_3**

T. Hirvikorpi, M. Vähä-Nissi, J. Nikkola, A. Harlin & M. Karppinen, *Surf. Coat. Technol.* 205, 5088 (2011).



CICADA WING

- Peculiar surface-nanostructure

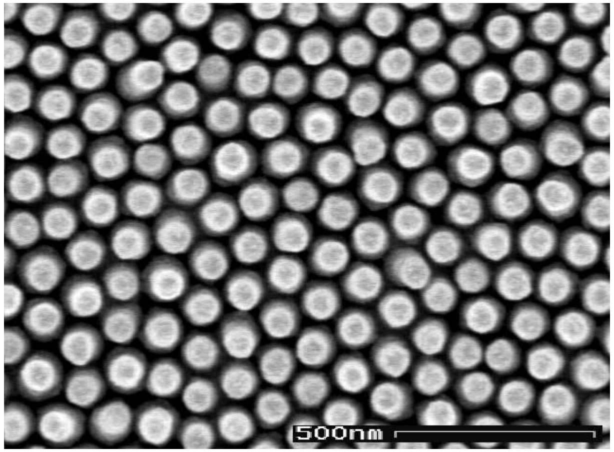
  200-nm high nanopillars coated with a waxy layer
- superhydrofobic

ZnO

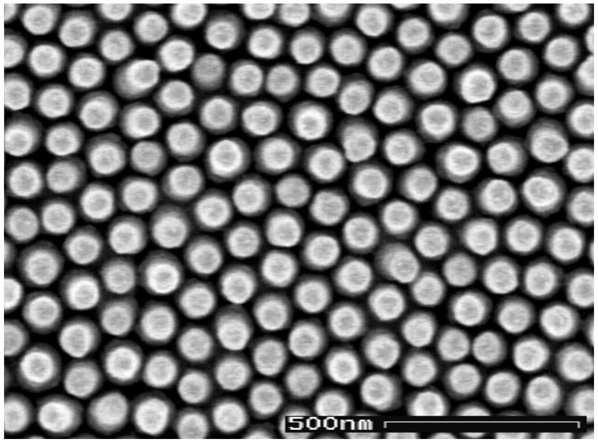
- Reversible change from hydrofobic to hydrophilic upon UV-radiation

CICADA WING + ZnO

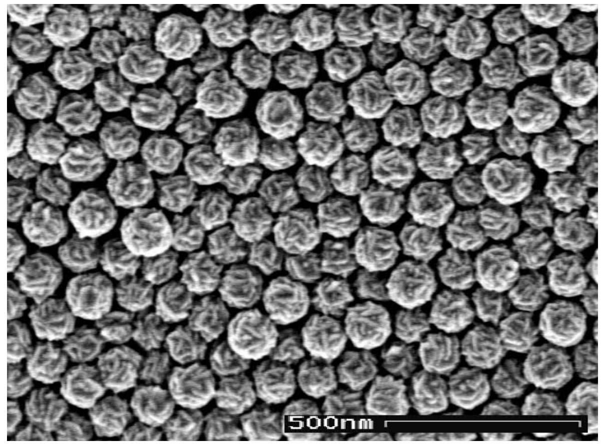
- Conformal coating of the wing by a thin layer of ZnO (~20 nm) by means of ALD
- Reversible change from superhydrofobic to superhydrophilic upon UV-radiation



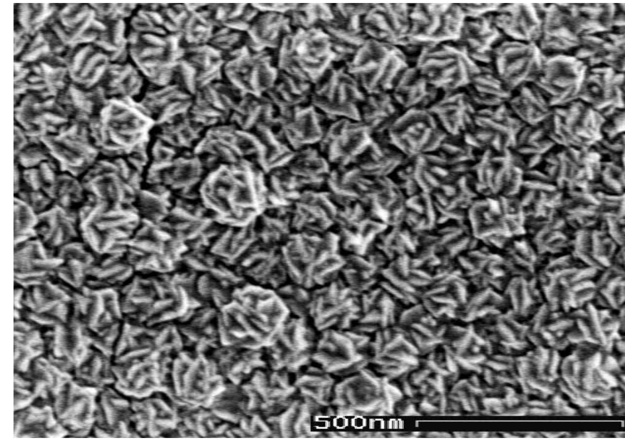
J. Malm, E. Sahramo, M. Karppinen & R. Ras, *Chem. Mater.* **22**, 3349 (2010).



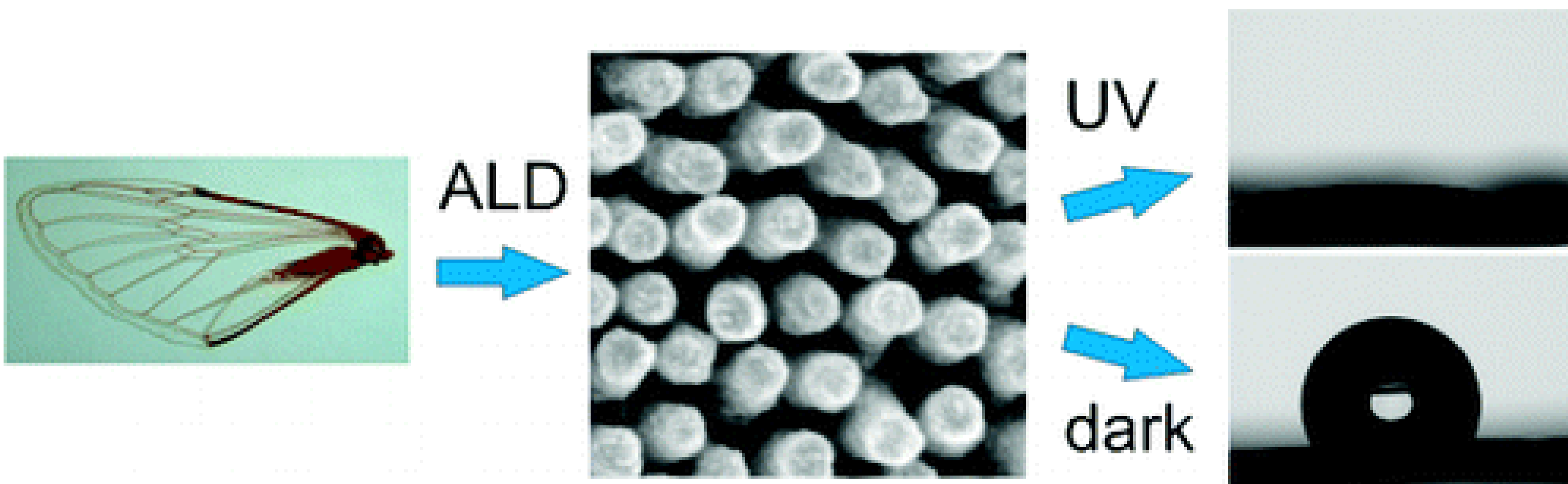
100 cycles (20 nm)

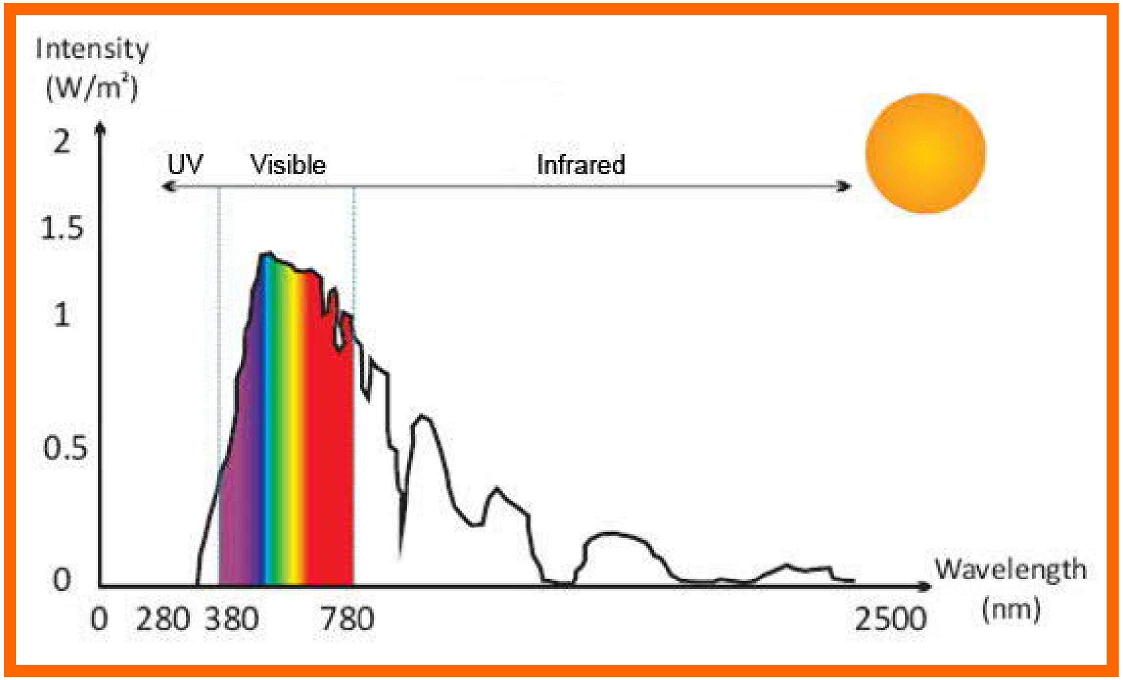


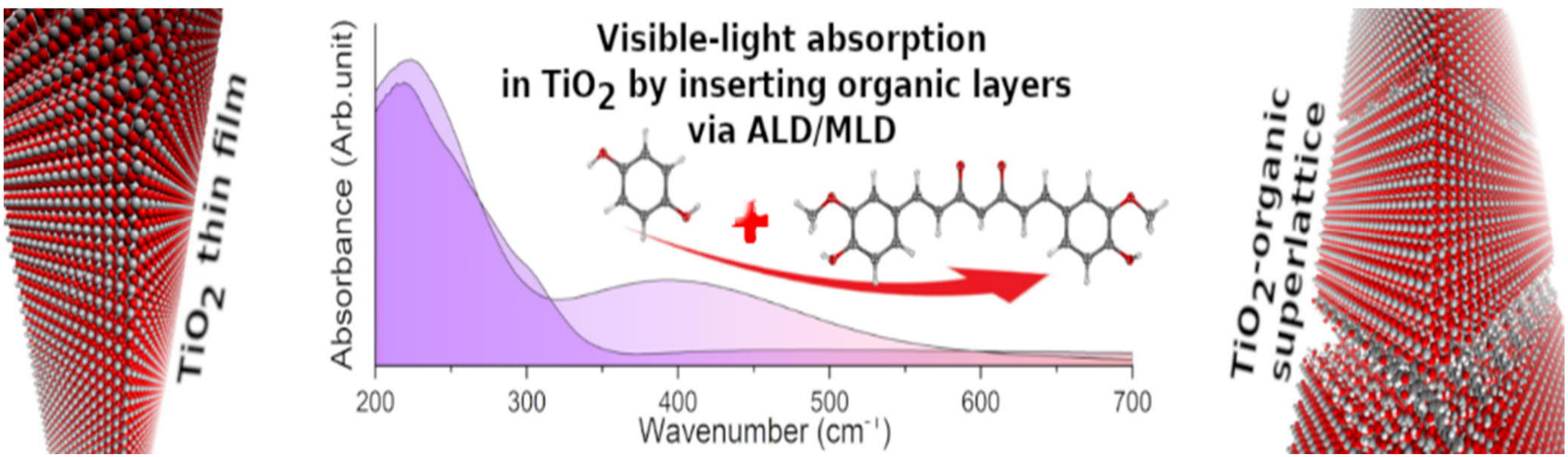
300 cycles (60 nm)



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).