LECTURE SCHEDULE

	Date		Topic
1.	Wed	28.10.	Course Introduction & Short Review of the Elements
2.	Fri	30.10.	Periodic Properties & Periodic Table & Main Group Elements (starts)
3.	Fri	06.11.	Short Survey of the Chemistry of Main Group Elements (continues)
4.	Wed	11.11.	Ag, Au, Pt, Pd & Catalysis (Antti Karttunen)
5.	Fri	13.11.	Redox Chemistry
6.	Mon	16.11.	Transition Metals: General Aspects & Crystal Field Theory
7.	Wed	18.11.	Zn, Ti, Zr, Hf & Atomic Layer Deposition (ALD)
8.	Fri	20.11.	V, Nb, Ta & Metal Complexes and MOFs
9.	Mon	23.11.	Cr, Mo, W & 2D materials
10	Wed	25.11.	Mn, Fe, Co, Ni, Cu & Magnetism and Superconductivity
11.	Fri	27.11.	Resources of Elements & Rare/Critical Elements & Element Substitutions
12.	Mon	30.11.	Lanthanoids + Actinoids & Pigments & Luminescence & Upconversion
13.	Wed	02.12.	Inorganic Materials Chemistry Research

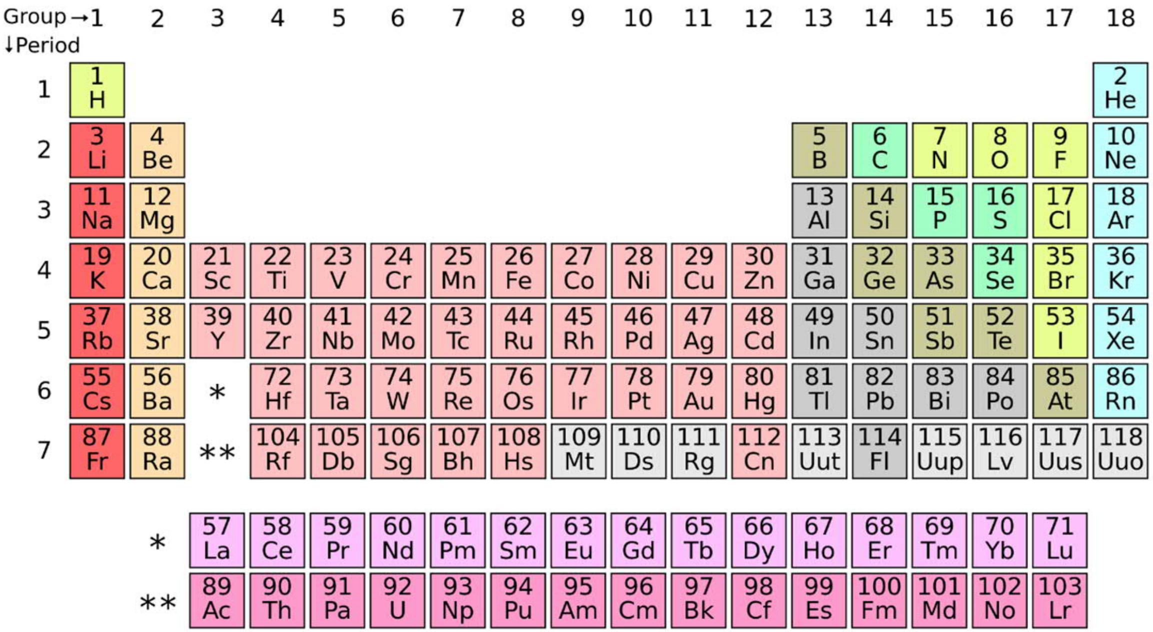
EXAM: Thu Dec 10, 9:00-12:00 Ke1

PRESENTATION TOPICS/SCHEDULE

Wed	**18.11.**	**Ti: Ahonen & Ivanoff**
Mon	**23.11.**	**Mo: Kittilä & Kattelus**
Wed	**25.11.**	**Mn: Wang & Tran**
		Ru: Mäki & Juopperi
Fri	**27.11.**	**In: Suortti & Räsänen**
		Te: Kuusivaara & Nasim
Mon	**30.11.**	**Eu: Morina**
		U: Musikka & Seppänen

QUESTIONS: Lecture 7

- **Why Zr and Hf are of the same size ? Give an example of the consequence of the same size.**
- **Which of the four elements (Zn, Ti, Zr, Hf) forms compounds at oxidation state +III ?**
- **Coordination number preferences of Zn, Ti, Zr and Hf in their oxides ?**
- **Which element can be used as a substituent to enhance electrical conductivity of ZnO ? Would the conductivity be of n- or p-type ?**
- **Which element can be used as a substituent to create oxygen vacancies in ZrO_2 ? Why ?**
- **How thin is a thin film ?**
- **Why in ALD technique: - film thickness control is straightforward ?**
  - 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+}	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^6\ 5s^2\ 4d^{10}\ 5p^6\ 4f^{14}$

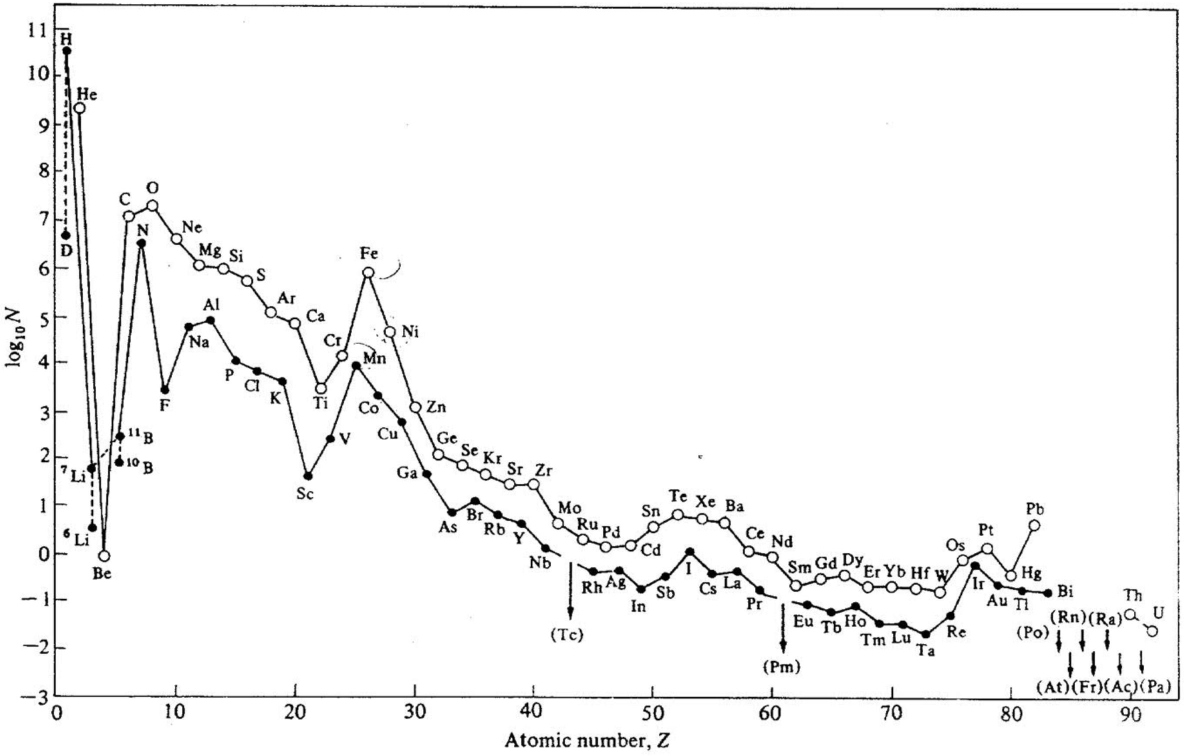
IONIC RADII (in Å)

		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 in use (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**: ref. to the seminar presentation ?
- **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)**

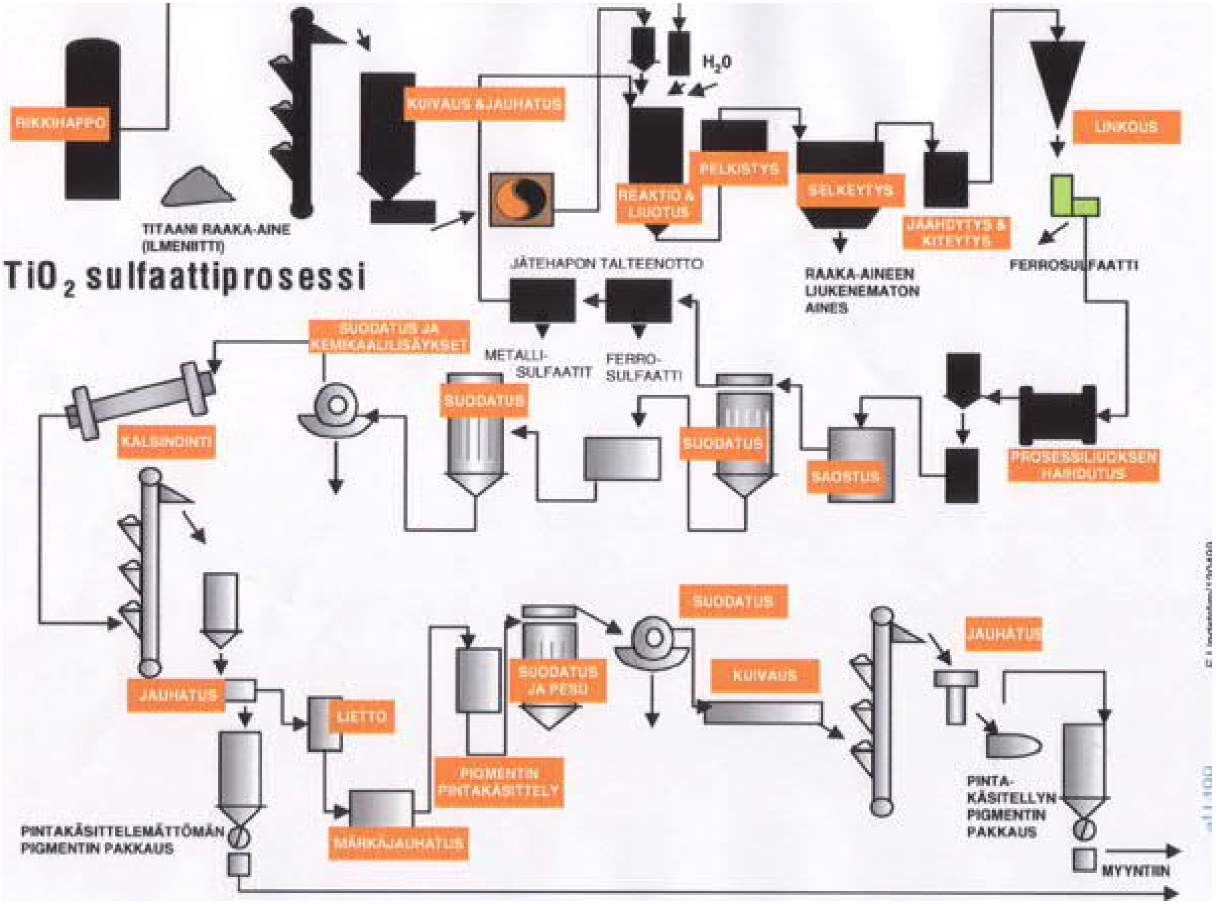
PRODUCTION OF TITANIUM

- 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:

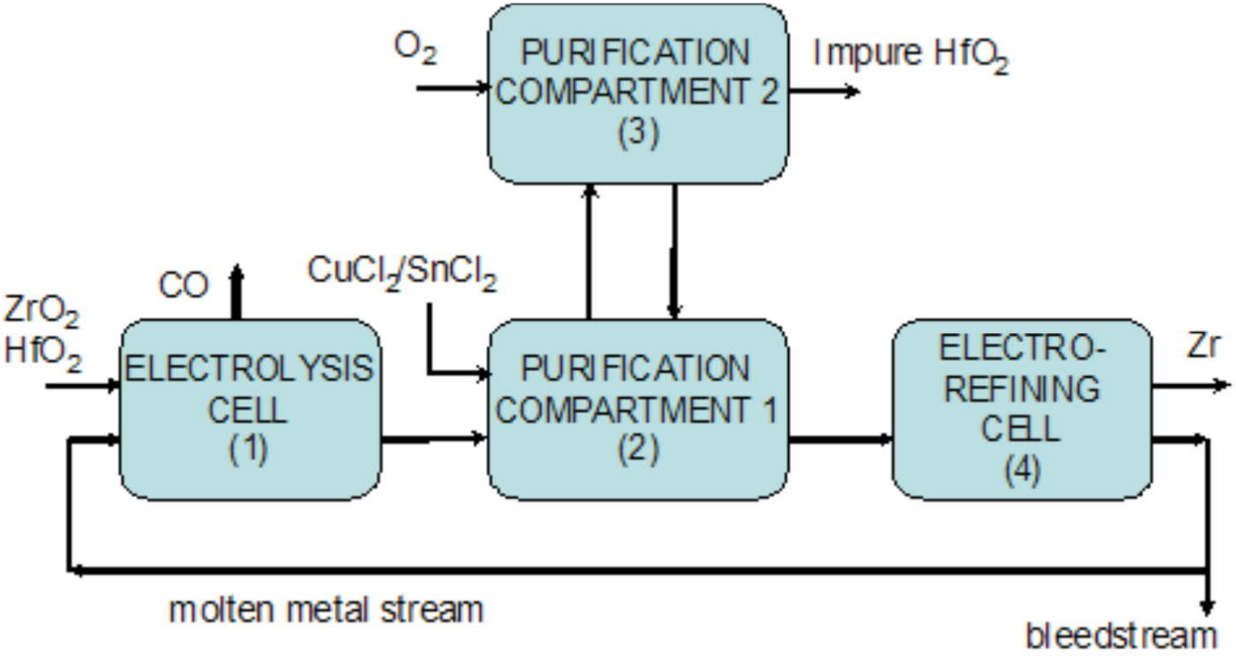
Raaka-aine (rutiili) kloorataan, jolloin muodostuu titaanitetrakloridia. Tetrakloridi hapetetaan (hapella) kaasufaasissa titaanidioksidiksi ja pintakäsitellään kuten sulfaattiprosessissakin. Kloridiprosessilla valmistetaan vain rutiilirakenteen omaavaa titaanidioksidia.

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

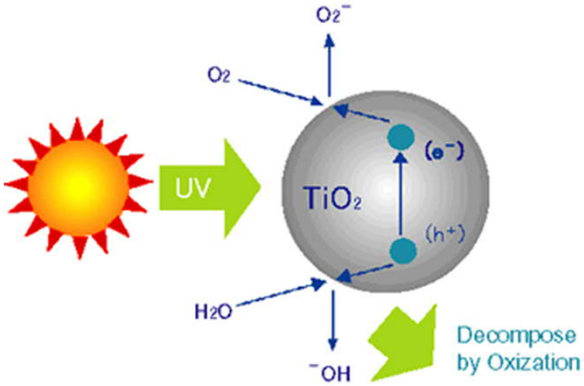


Role of Zinc in the structure and function of proteins

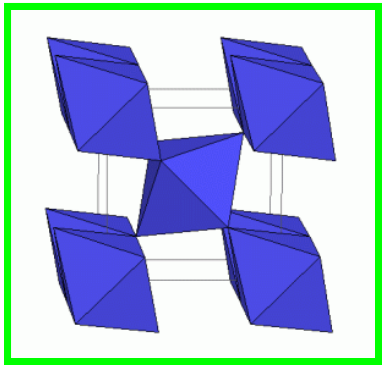
- Required for essential catalytic functions in enzymes
- Stabilizes the folding of protein subdomains
- Why Zinc ?
  - **widely available** in environment
  - **fixed oxidation state** (+II): completely resistant to redox changes and thus not affected by redox potentials in the organisms
  - prefers **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

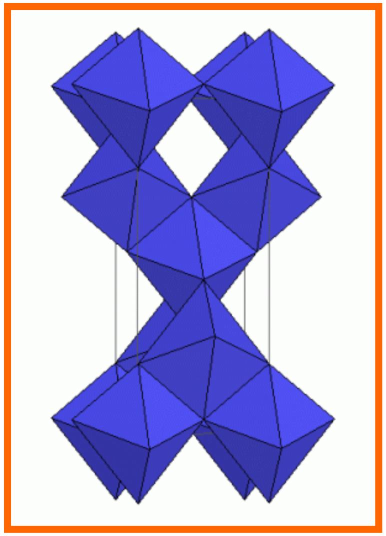
TiO_2

Crystal structures:	- **rutile**, **anatase**, brokite
Large refractive index:	- most important white pigment: paints, paper, plastics, cosmetics, foods, tooth pastes, …
UV protection:	- sunscreens, plastics
Inert:	- filler material in pharmaceuticals
Photocatalytic:	- Akira Fujishima 1970s - water splitting - decomposition of organics with UV light - antibacterial effect: 3-times stronger compared to chlorine 1.5-times stronger compared to ozone



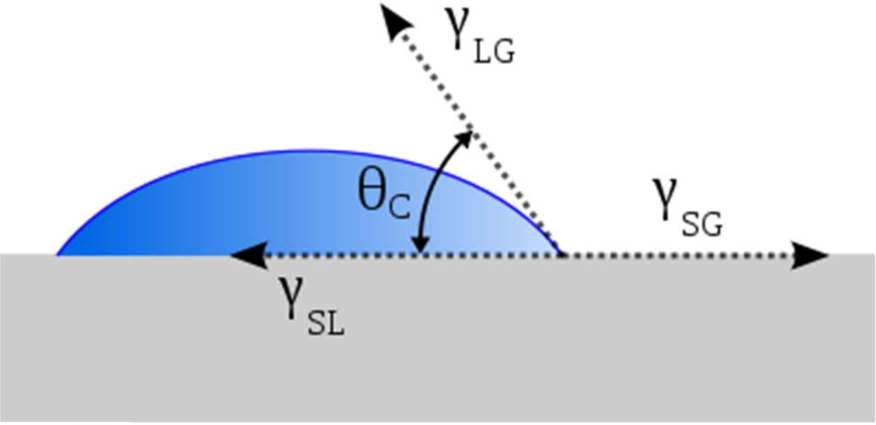
Superhydrophilic:	- Akira Fujishima 1996 - after UV radiation - water does not form droplets but spreads on TiO_2 surfaces for a thin surface layer - e.g. sauna mirrors

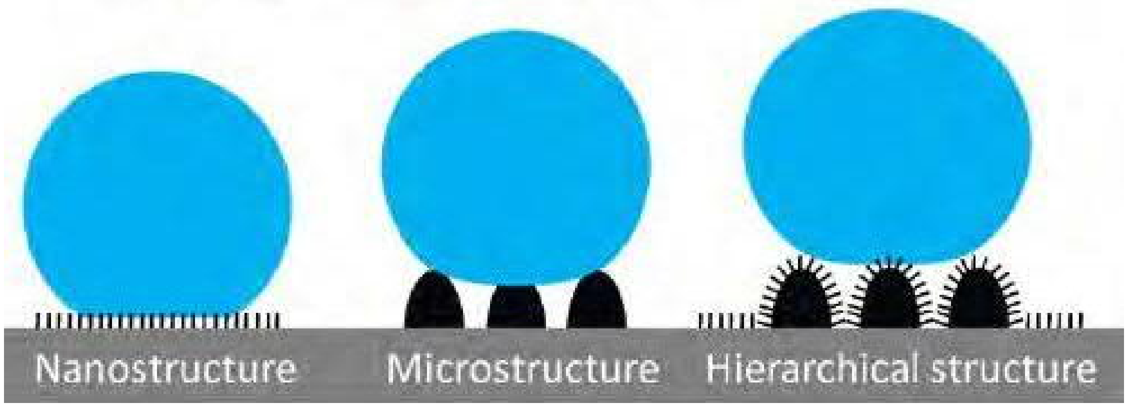




SUPERHYDROPHOBICITY

- 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°

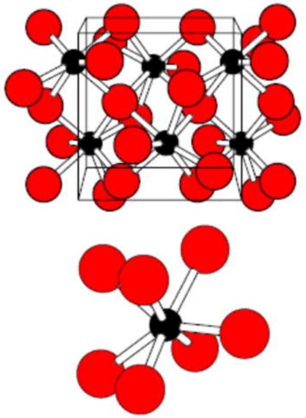




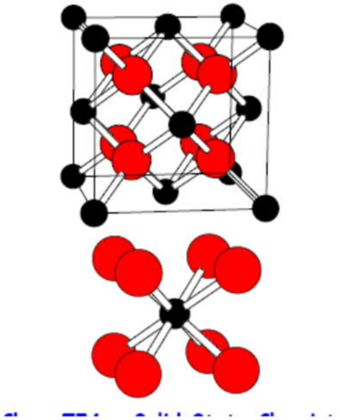
ZrO_2

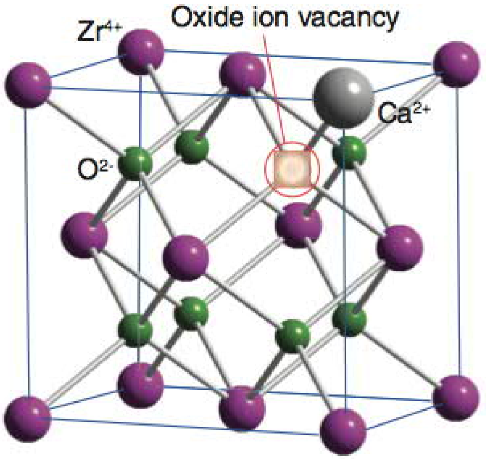
- Used as industrial ceramics, protective coating (e.g. on TiO_2 pigment particles) and refractory material in e.g. insulation
- 7-coordinated (monoclinic) structure at RT &
  8-coordinated cubic structure at high temperatures
- Y^{III}-forZr^{IV} substitution stabilizes the cubic ZrO_2 structure synthesized 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 ($Y^{3+} \rightarrow Zr^{4+}$ → oxygen vacancies)

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



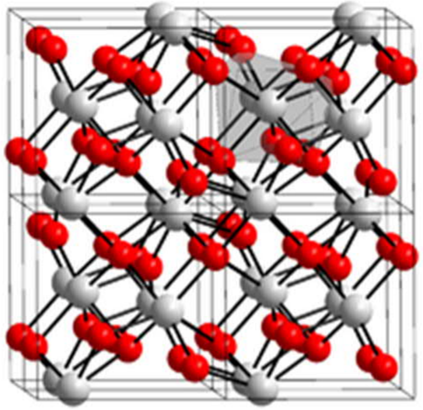
High Temperature
Cubic (Fm3m)
cubic coordination for Zr
tetrahedral coord. for O^{2-}





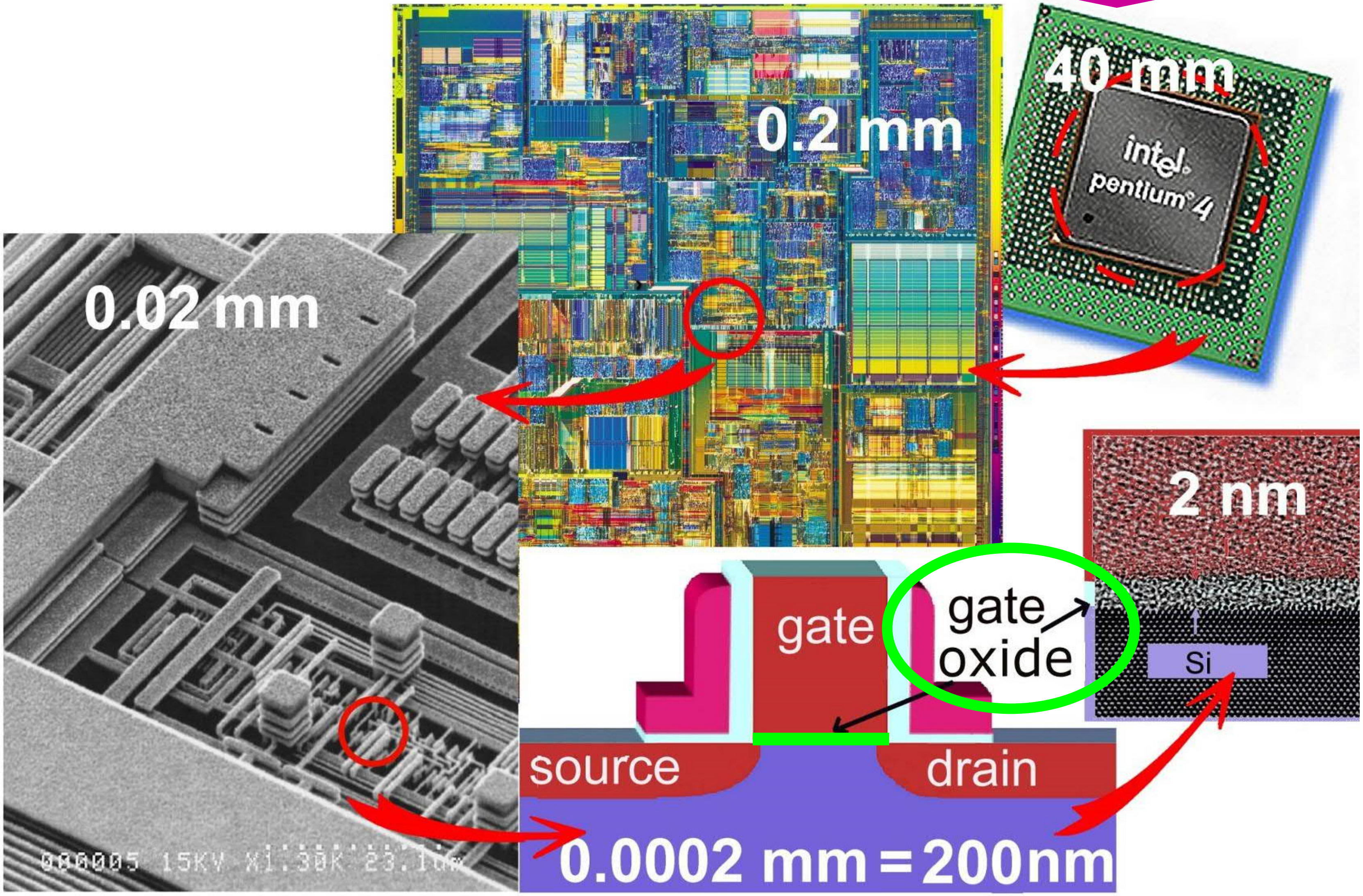
HfO_2

- Similar (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

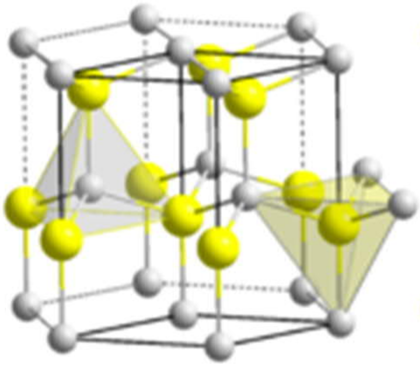
smaller transistors → lower gate voltage
same electric fields → thinner dielectric
SiO_2 → **HIGH-*k* DIELECTRICS**

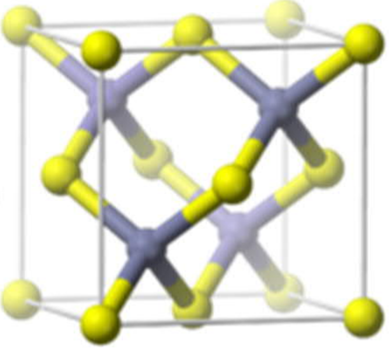


ZnO

- 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/hydrogen or oxygen vacancies/ → n-type doping
- Al^{3+}-for-Zn^{2+} doping for enhanced n-type doping
- Attractive properties for optoelectronics: wide bandgap, tunable electrical properties, high transparency, high electron mobility

→ emerging applications in transparent electrodes, liquid crystal displays, energy-saving and heat-protecting windows, electronics as thin-film transistors and light-emitting diodes





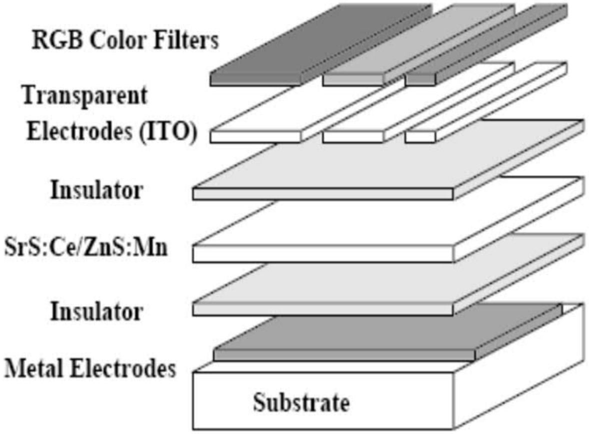
OXIDES (Al_2O_3, ZnO, TiO_2, ZrO_2 & HfO_2) & ALD (atomic layer deposition) thin-film technology

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

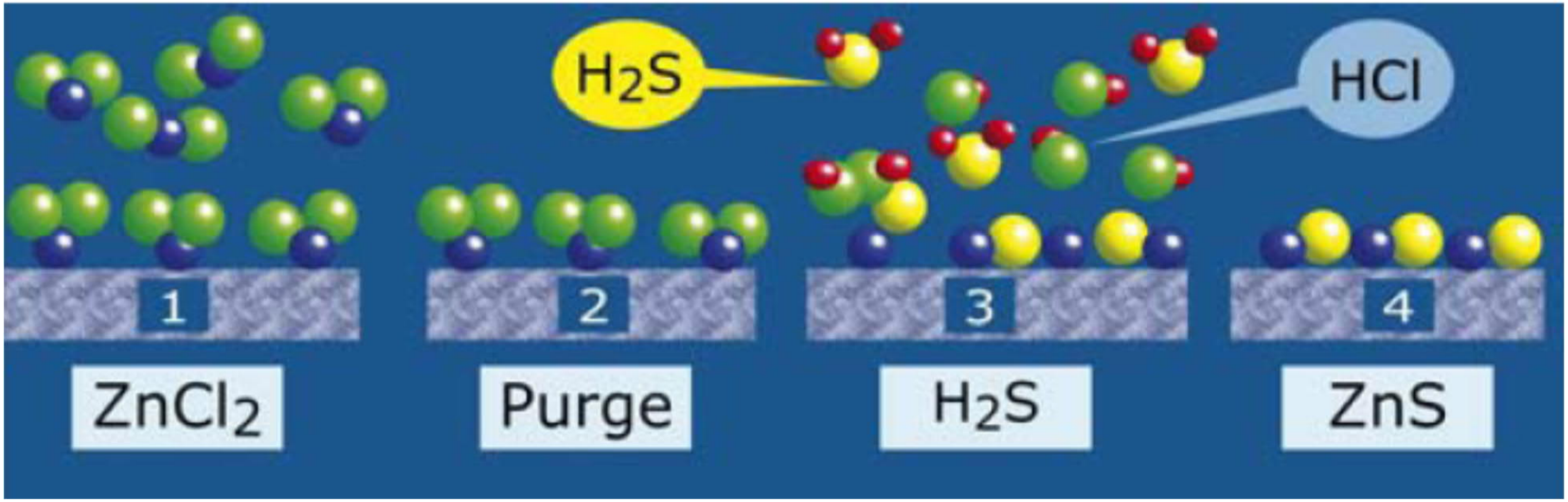
Atomic Layer Deposition (ALD) Thin-Film Technique

- **Gaseous precursors**
- **Self-limiting surface reactions**
- **Conformal, homogeneous thin films with atomic-layer accuracy**



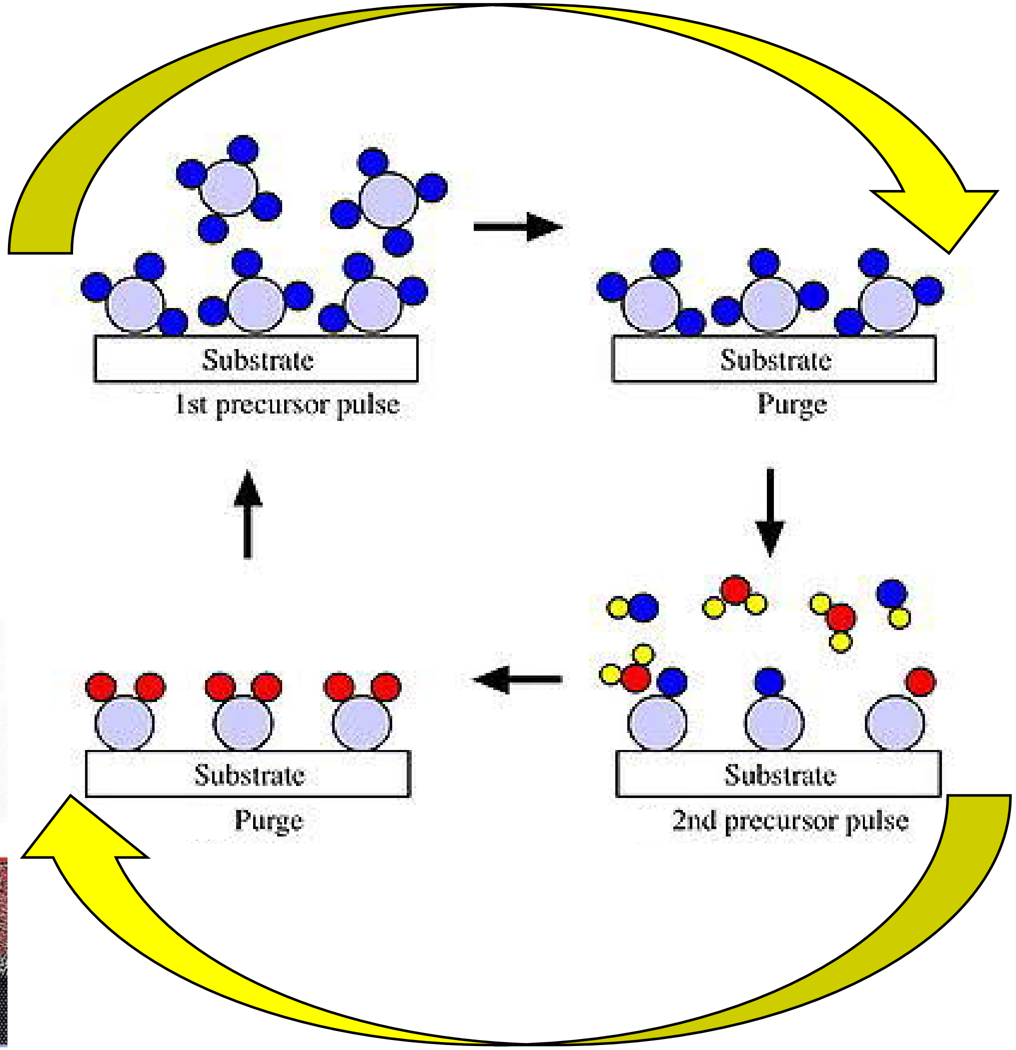
Electroluminescent display

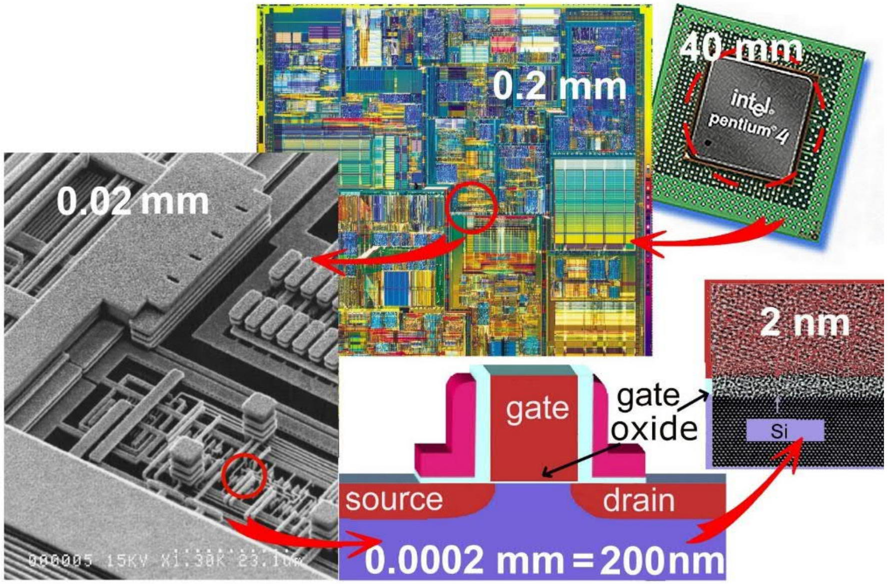
Instrumentarium / Finlux / Planar



HfO_2-ALD
$HfCl_4 + H_2O$

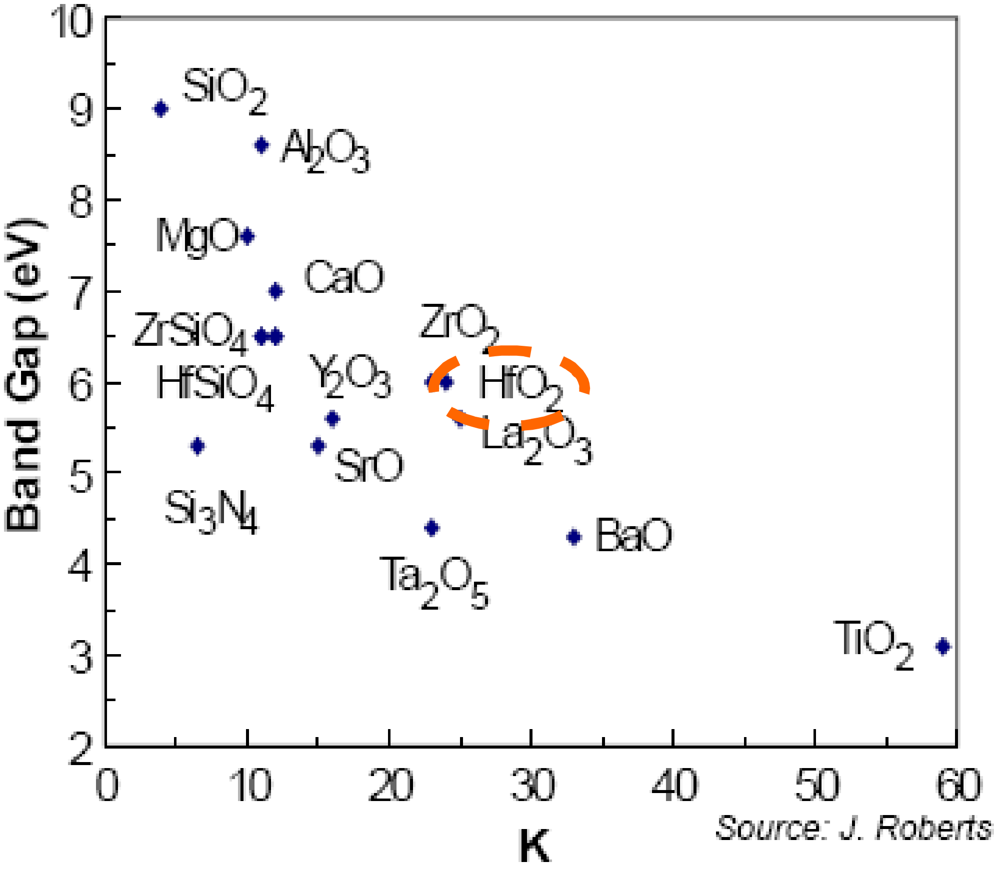
ALD cycle





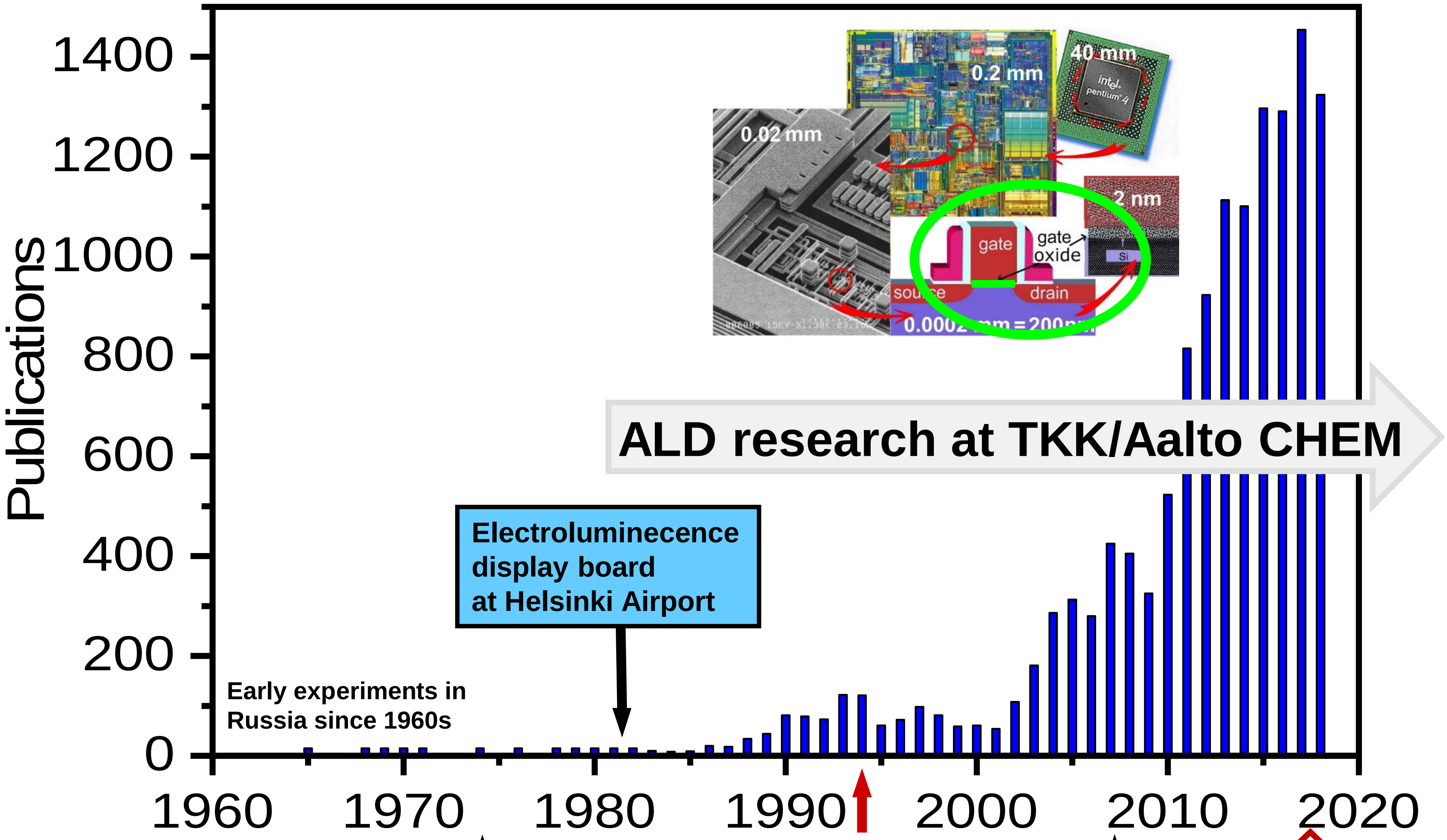
Conditions for high-*k* dielectrics

- **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)



ALD research at TKK/Aalto CHEM

Early experiments in Russia since 1960s

Electroluminecence display board at Helsinki Airport

ALD-HfO_2 process by Ritala & Leskelä

Tuomo Suntola: Patent filed 1974

ALD-HfO_2 by Intel for transistors

Millenium 2018 Prize for Suntola

Atomic Layer Deposition of Al_2O_3

- Al-$_{\text{source (precursor)}}$: $Al(CH_3)_3$
- Oxygen source (co-reactant): H_2O
- Substrate: Si

(1) Substrate surface is initially covered with hydroxyl (OH) groups

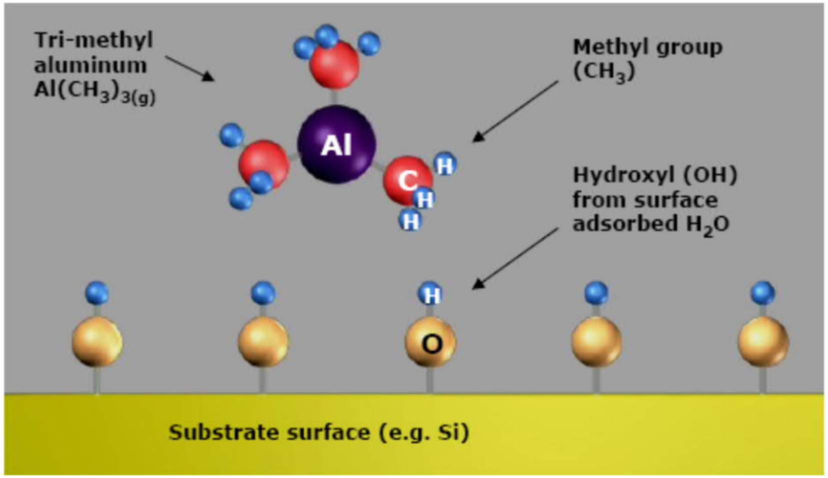
First trimethyl aluminum [TMA: $Al(CH_3)_3$] is pulsed into the reactor

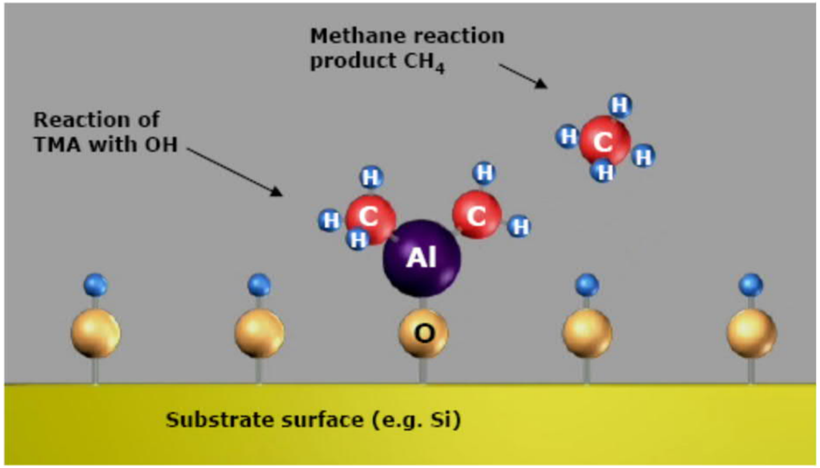
(2) TMA reacts with the surface OH groups, producing methane (CH_4) as a byproduct

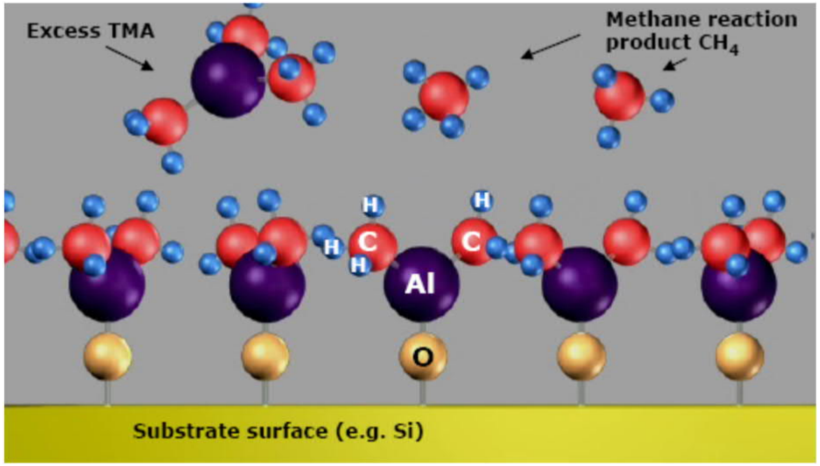
(3) Reaction continues until the surface is passivated (= covered with a TMA layer)

TMA does not react with itself: this terminates the reaction to one layer

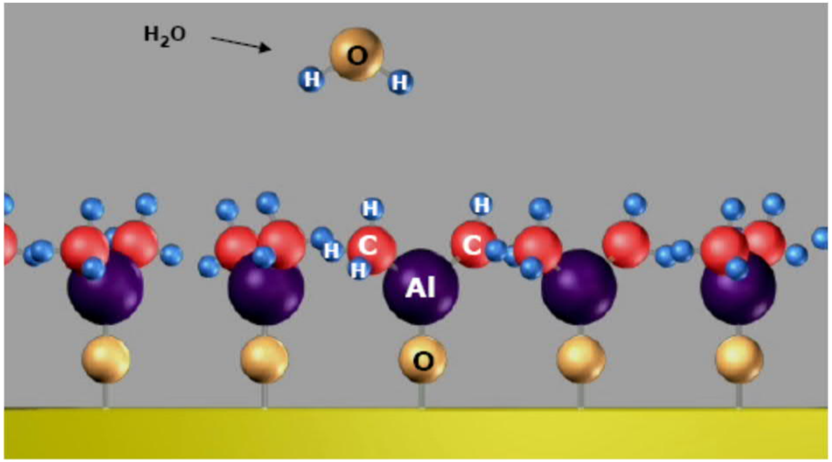
Excess TMA and methane molecules are pumped away (purged with an N_2 pulse)







(4) Next, water vapour (H_2O) is pulsed into the reaction chamber

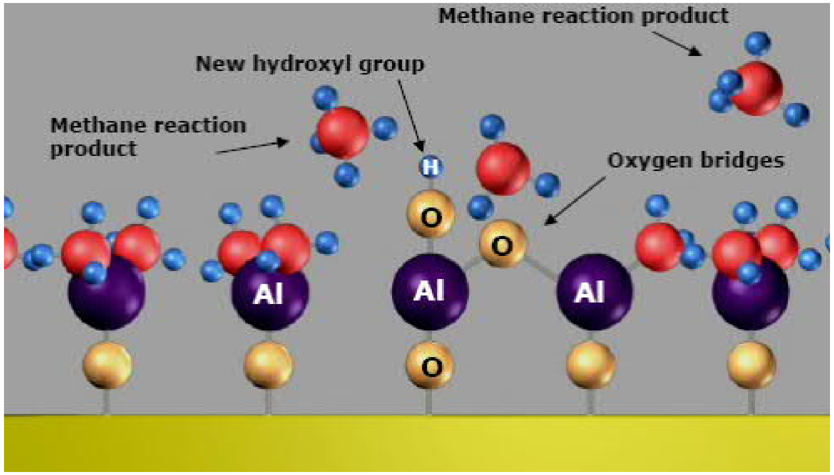


(5) Water reacts with the surface methyl (CH_3) groups, forming Al-O bonds and surface OH groups

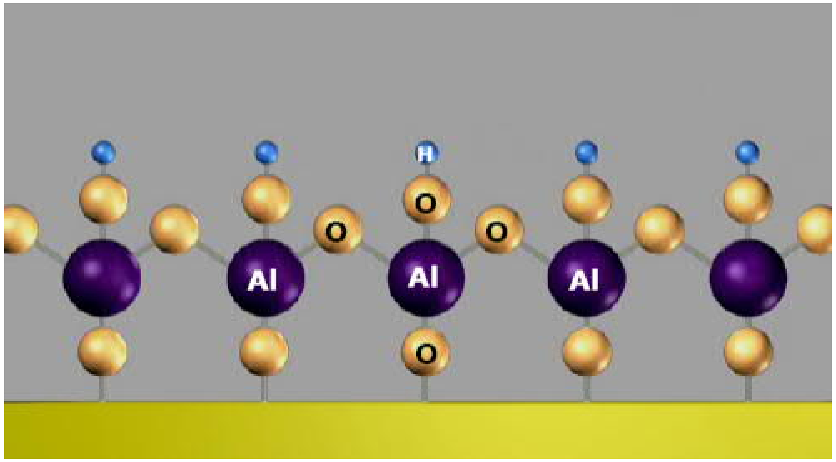
Again methane is the byproduct

Reaction continues until the surface is passivated

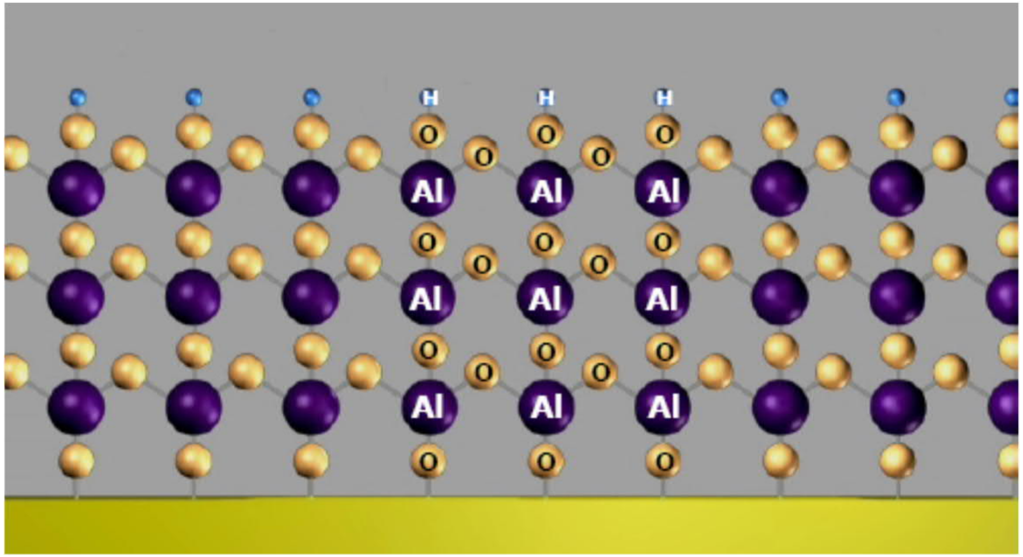
Again the reaction is self-limited to one new layer
(as H_2O does not react with itself)



(6) Excess H_2O and CH_4 molecules are pumped away (purged with an N_2 pulse)



- One TMA pulse (+ N_2 purge) and one H_2O pulse (+ N_2 purge) form one ALD cycle, producing one layer of Al_2O_3 (of *ca*. 1 Å in thickness)
- Here the outcome of three ideal ALD cycles is shown
- Each cycle takes approximately 5 to 10 seconds

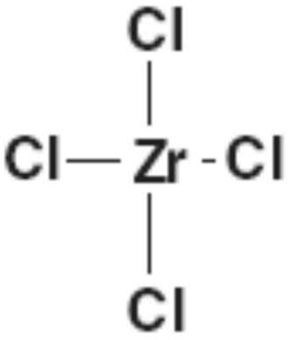


www.cambridgenanotech.com

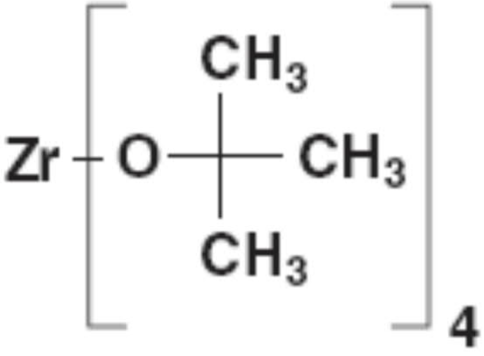
Reaction-1: $(Si/Al)\text{-}OH\,(s) + Al(CH_3)_3\,(g) \rightarrow (Si/Al)\text{-}O\text{-}Al(CH_3)_2\,(s) + CH_4\,(g)$

Reaction-2: $(Si/Al)\text{-}O\text{-}Al(CH_3)_2\,(s) + 2\,H_2O\,(g) \rightarrow (Si/Al)\text{-}O\text{-}Al(OH)_2\,(s) + 2\,CH_4\,(g)$

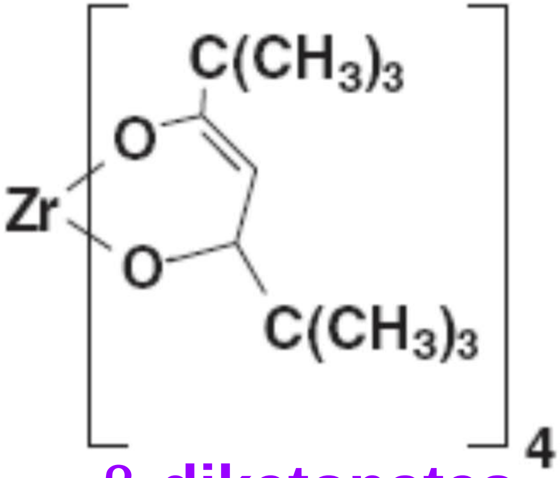
COMMON PRECURSORS in ALD



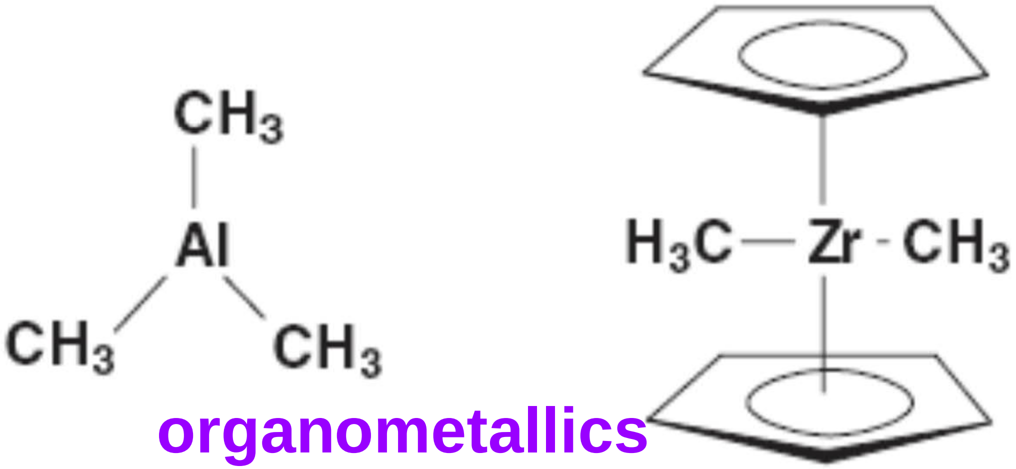
halides



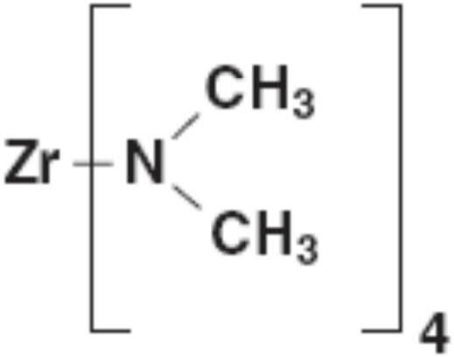
alkoxides



β-diketonates



organometallics



amido complexes

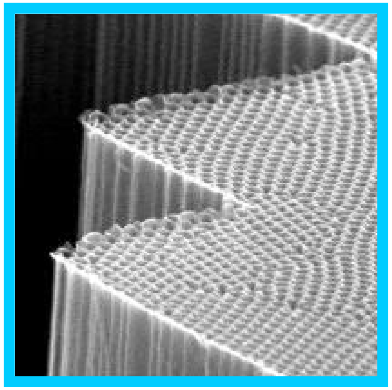
e.g. cyclopentadienyls

Advantages of ALD

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

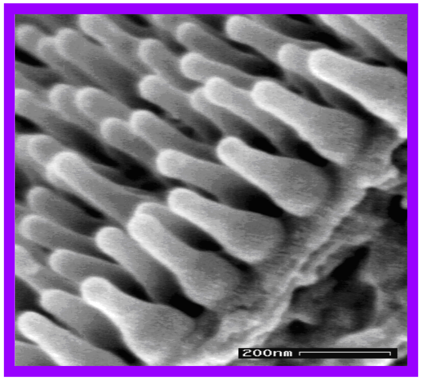
ELECTRONICS

- Excellent conformality



NANO

- Low deposition temperature
- Gentle deposition process



BIO

- Organic/polymer films
- Inorganic/organic hybrid materials

NEW

Kalevala Koru (Finland):

- **traditional silver jewelry**

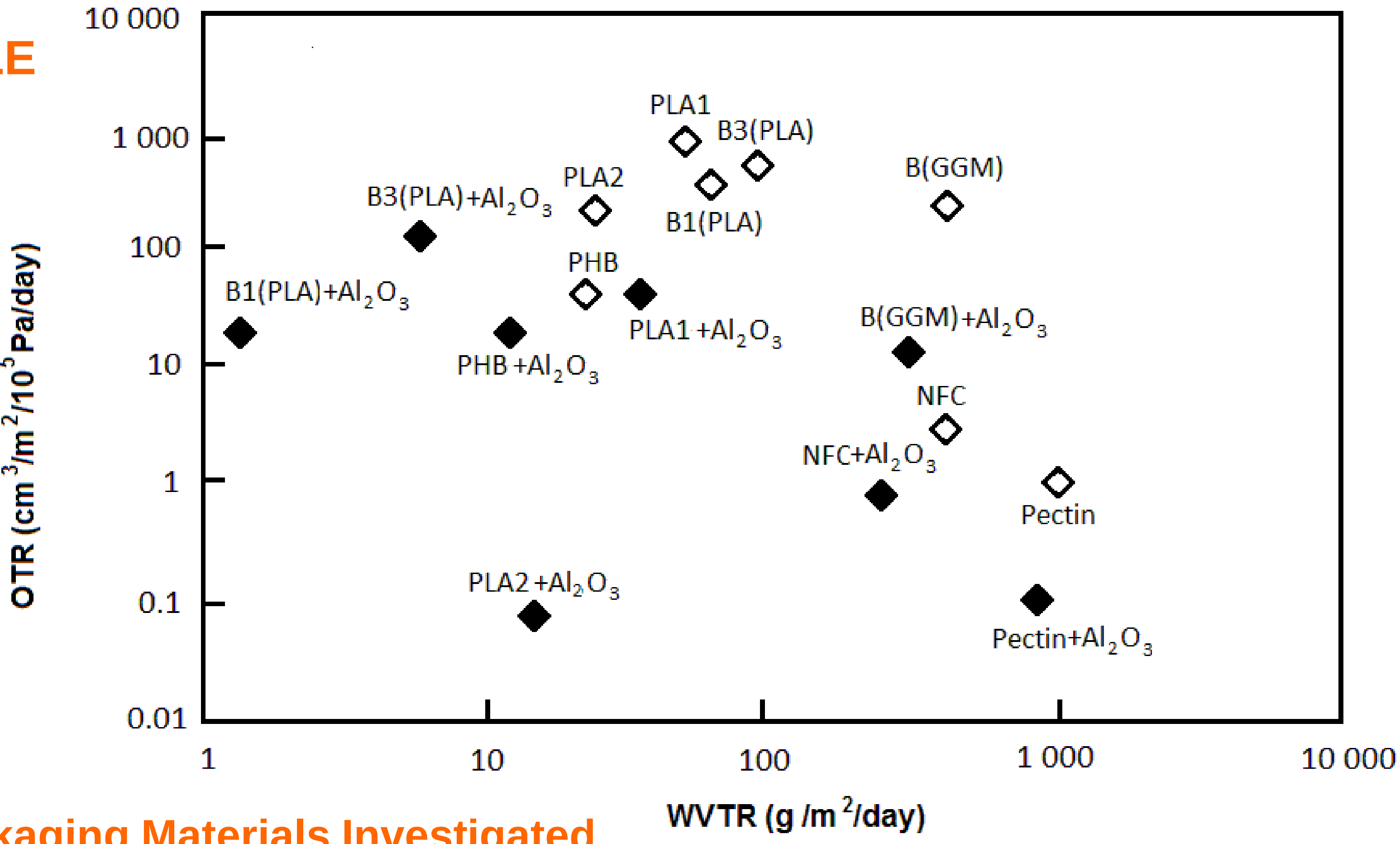
Beneq (Finland):

- **Al_2O_3 coating by ALD**

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

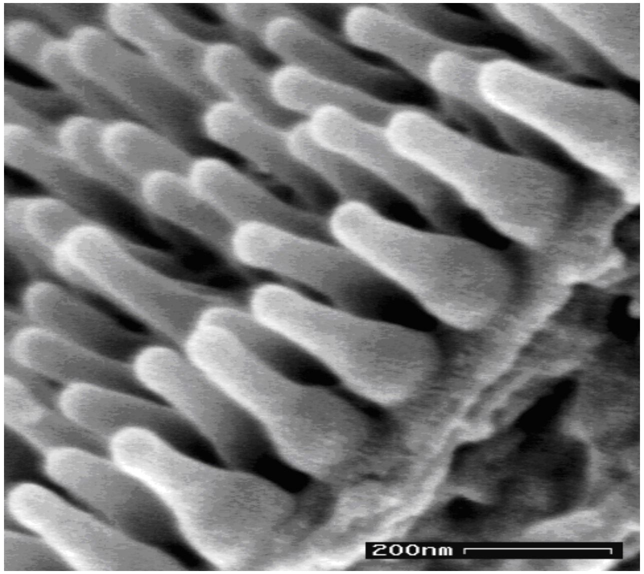
B(PLA)	**Polylactide-coated board**
PLA	**Polylactide film**
NFC	**Nano-fibrillated cellulose film**
B(GGM)	**Galactoclugomannan-coated board**
PHB	**Polyhydroxy butyrate film**
Pectin	**Pectin film made by solution casting**

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**

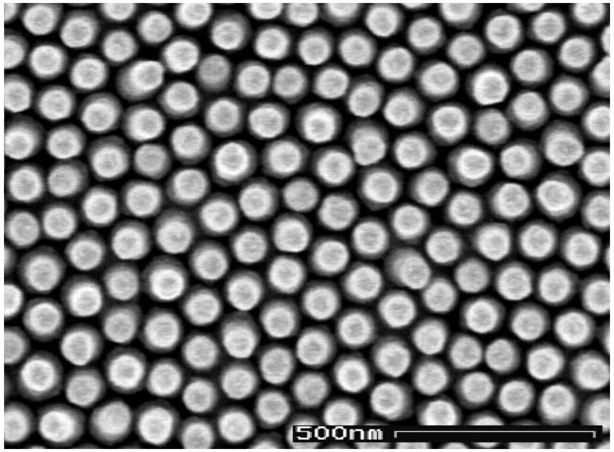
  200-nm high nanopillars coated with a waxy layer
- **superhydrofobic**

ZnO

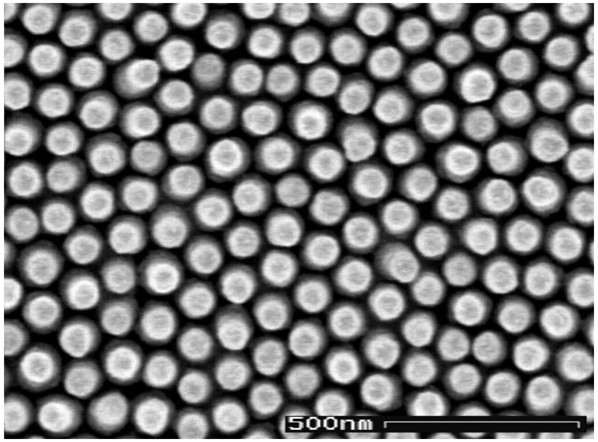
- **Reversible change from hydrofobic to hydrophilic upon UV-radiation**

CICADA WING + ZnO

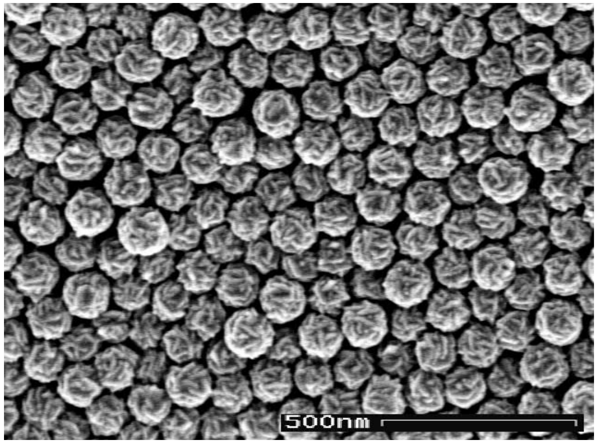
- **Conformal coating of the wing by a thin layer of ZnO (~20 nm) by means of ALD**
- **Reversible change from superhydrofobic to superhydrophilic upon UV-radiation**



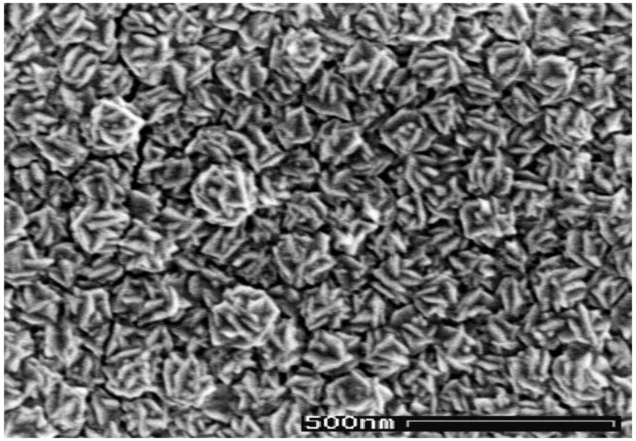
J. Malm, E. Sahramo, M. Karppinen & R. Ras, *Chem. Mater.* **22**, 3349 (2010).



100 cycles (20 nm)



300 cycles (60 nm)



500 cycles (100 nm)