Aalto University
School of Chemical
Engineering

ALD, MLD & ALD/MLD

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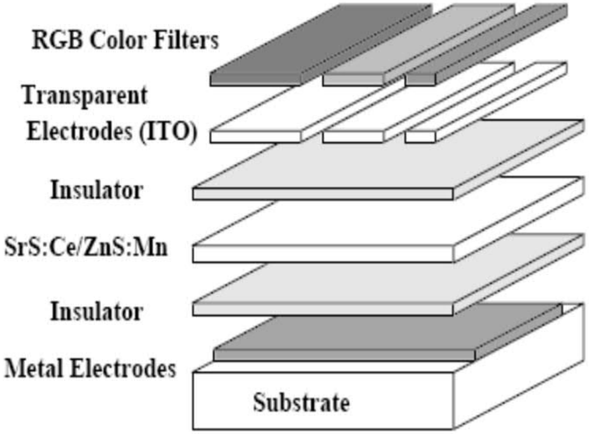
Surfaces & Films
4.11.2020

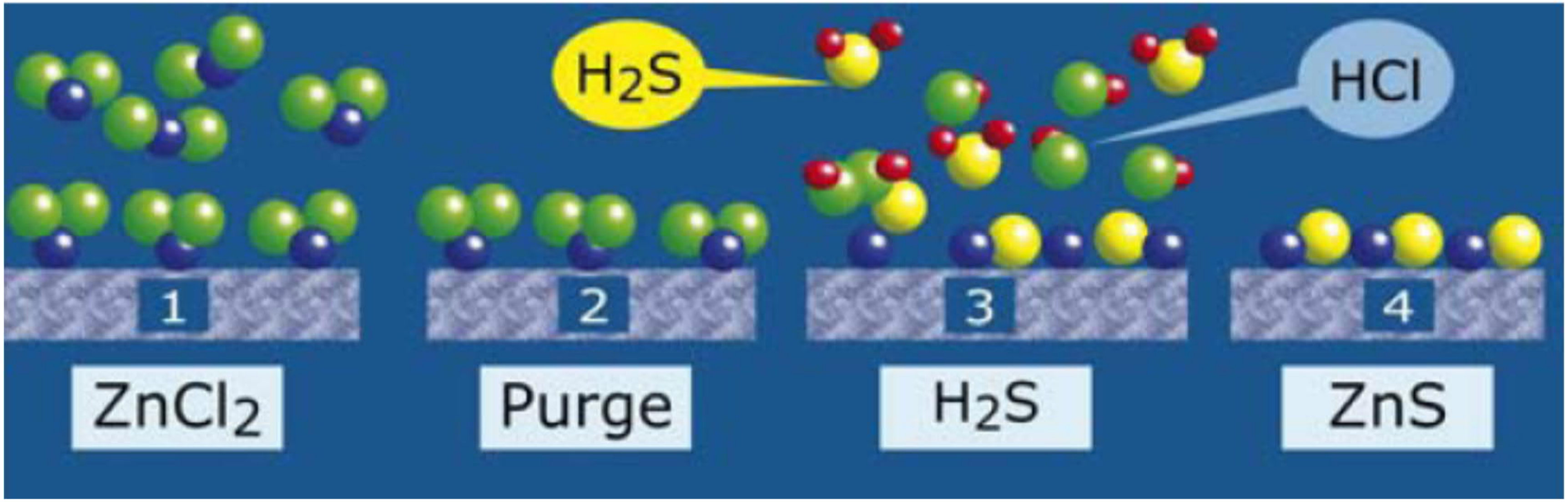
Atomic Layer Deposition (ALD) Thin-Film Technique

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



Electroluminescent display

Instrumentarium / Finlux / Planar



Prototype ALD thin films

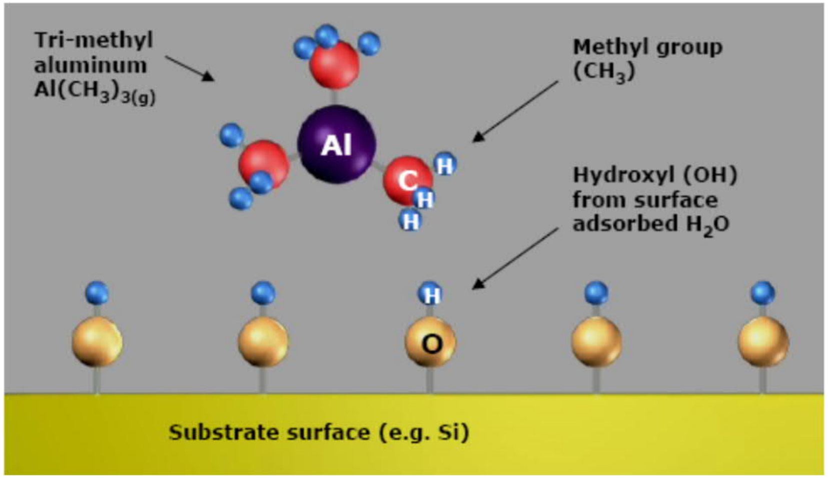
- ALD-Al_2O_3 (amorphous): barrier and protective coating
- ALD-HfO_2 (amorphous): high-k dielectrics
- ALD-ZnO (crystalline): semiconductor (e.g. thermoelectrics)
- ALD-TiO_2 (crystalline): e.g. photovoltaics

Atomic Layer Deposition of Al_2O_3 (AlO_x)

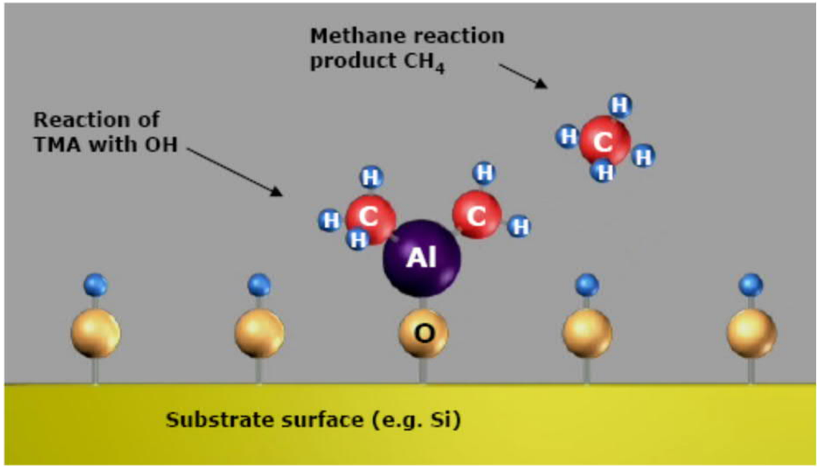
- **Al-source (precursor): $Al(CH_3)_3$**
- **Oxygen source (co-reactant): H_2O**
- **Substrate: Si**

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

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



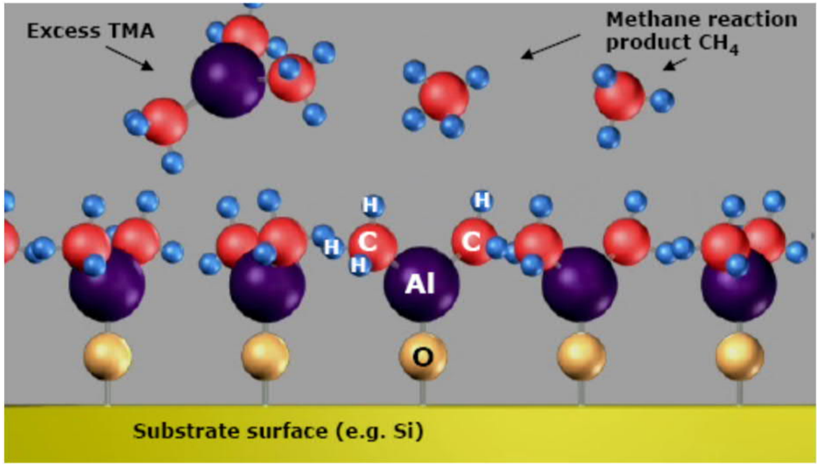
(2) TMA reacts with the surface OH groups, producing methane (CH_4) as a byproduct



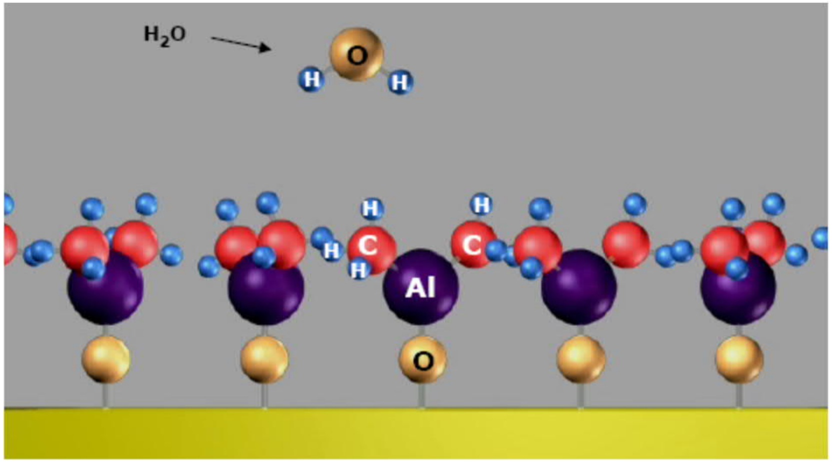
(3) Reaction continues until the surface is passivated (= covered with a TMA layer)

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

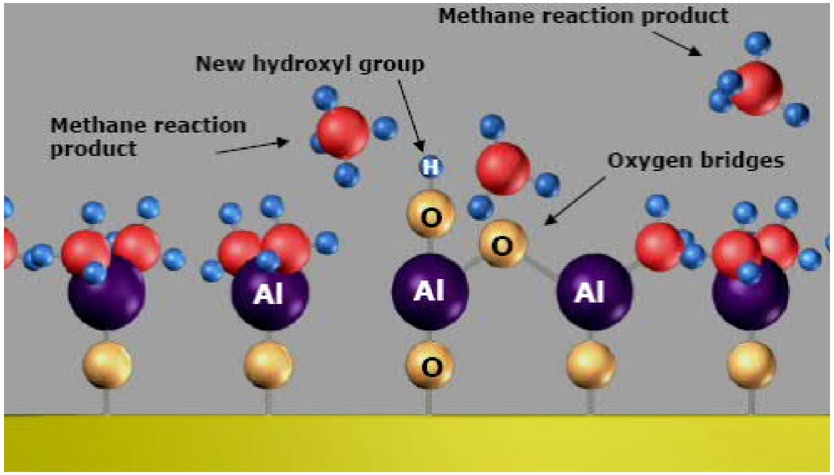


(5) Water reacts with the surface methyl (CH_3) groups, forming Al-O bonds and surface OH groups

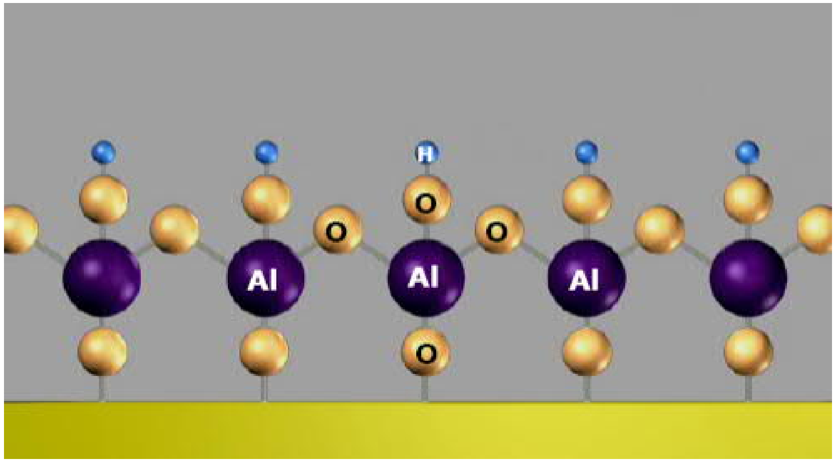
Again methane is the byproduct

Reaction continues until the surface is passivated

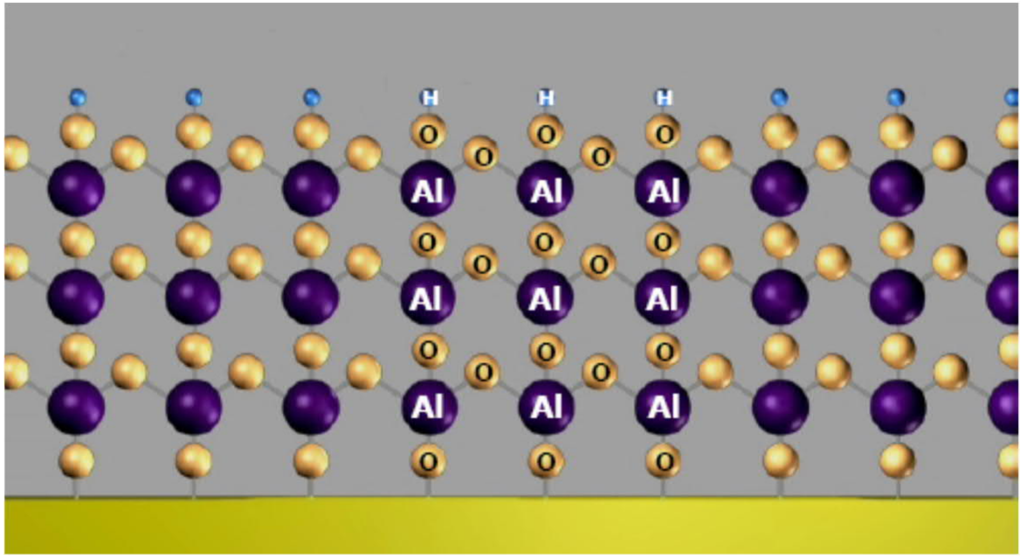
Again the reaction is self-limited to one new layer
(as H_2O does not react with itself)



(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

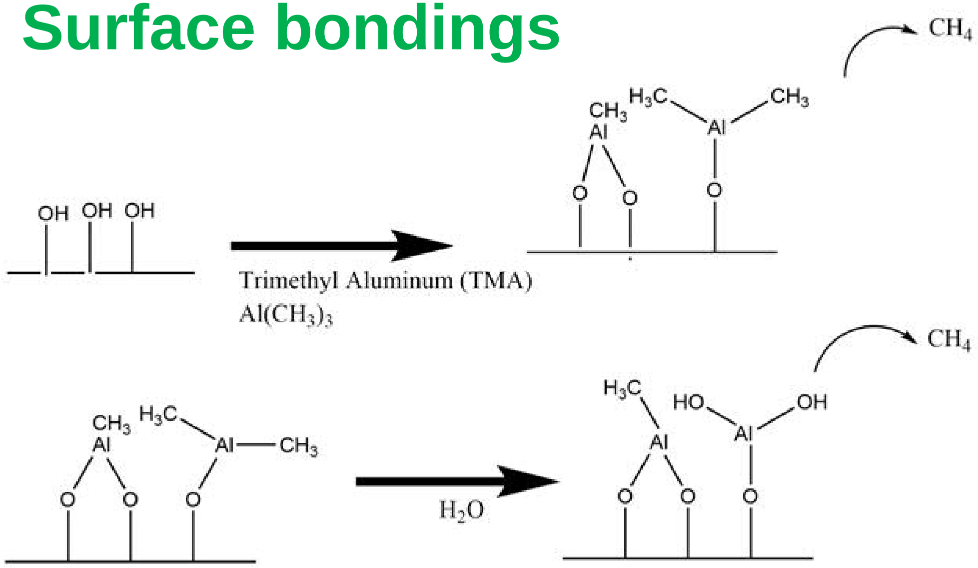


www.cambridgenanotech.com

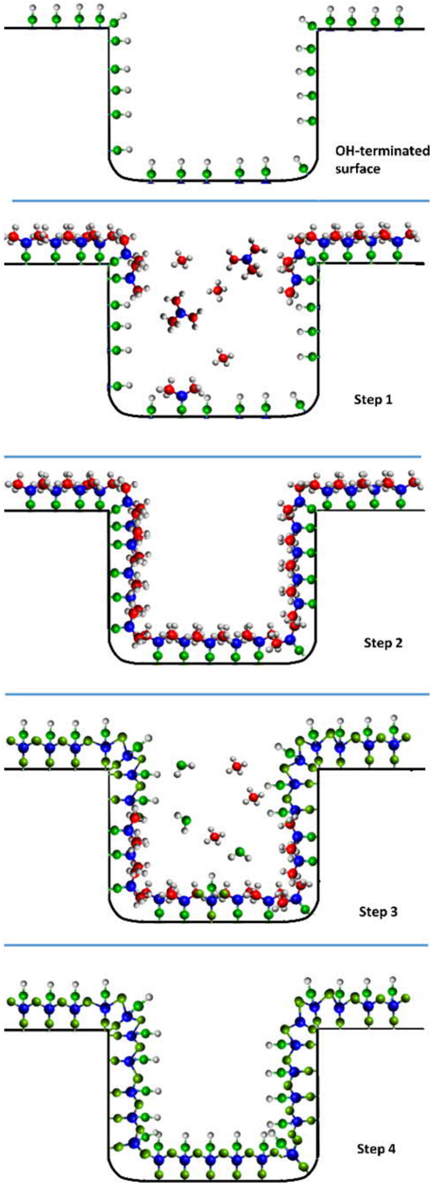
Reaction-1: $(Si/Al)\text{-}OH_{(s)} + Al(CH_3)_{3(g)} \rightarrow (Si/Al)\text{-}O\text{-}Al(CH_3)_{2(s)} + CH_{4(g)}$

Reaction-2: $(Si/Al)\text{-}O\text{-}Al(CH_3)_{2(s)} + 2H_2O_{(g)} \rightarrow (Si/Al)\text{-}O\text{-}Al(OH)_{2(s)} + 2CH_{4(g)}$

Surface bondings

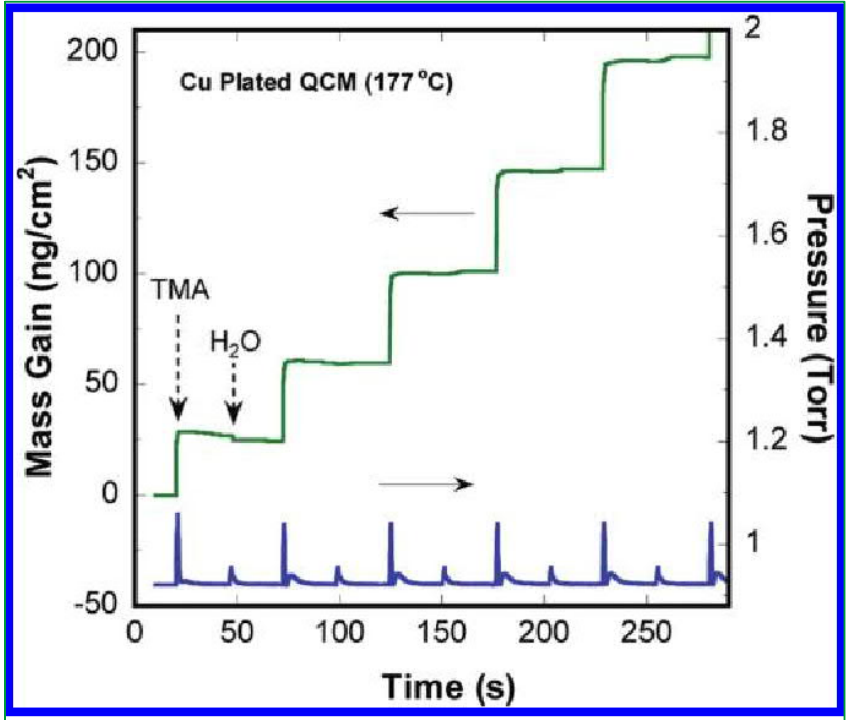


Conformal coating



In-situ QCM

(quartz crystal microbalance)



Kalevala Koru (Finland):

- **traditional silver jewelry**

Beneq (Finland):

- **Al_2O_3 coating by ALD**

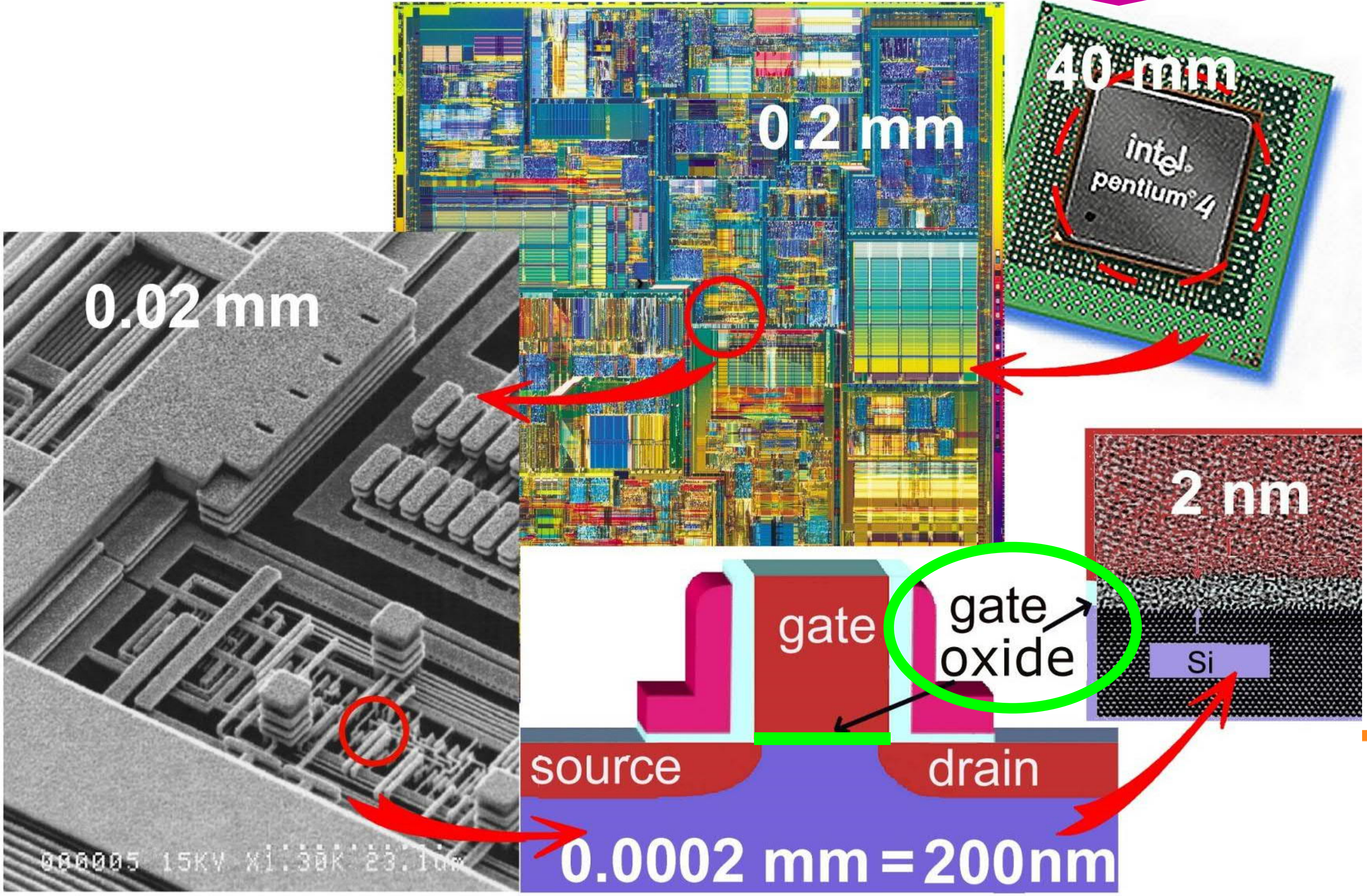
uncoated **Al_2O_3-coated**

BEFORE **AFTER TARNISHING TEST**

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

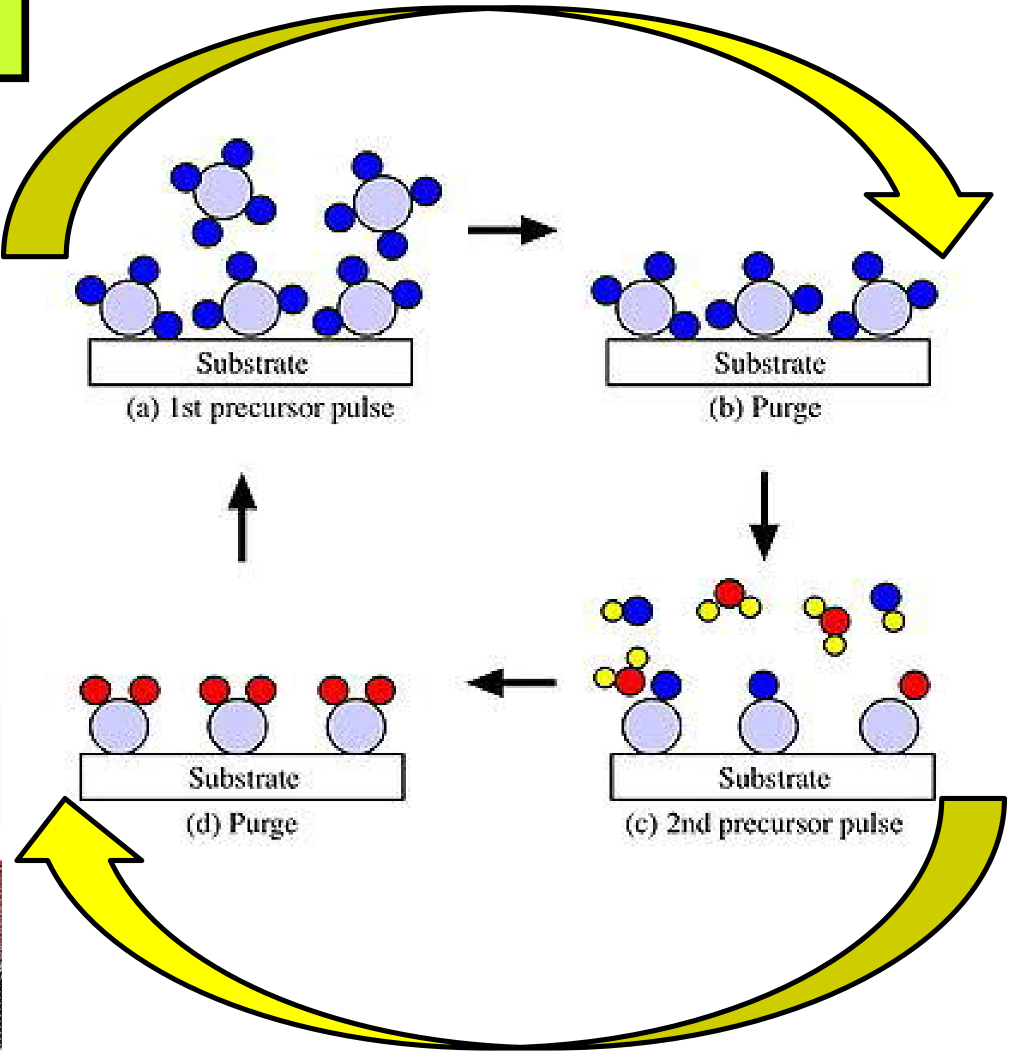
CMOS transistor

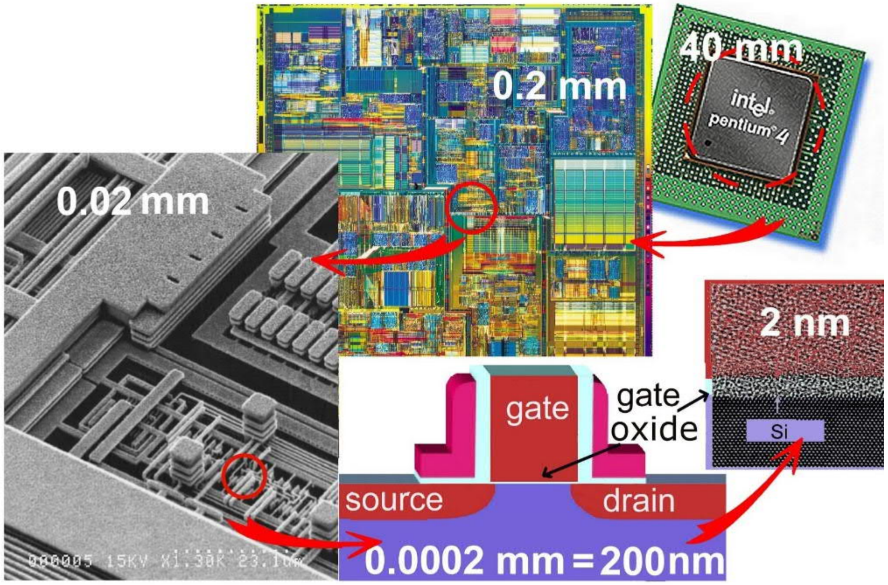
smaller transistors → lower gate voltage
same electric fields → thinner dielectric
SiO2 → HIGH-*k* DIELECTRICS

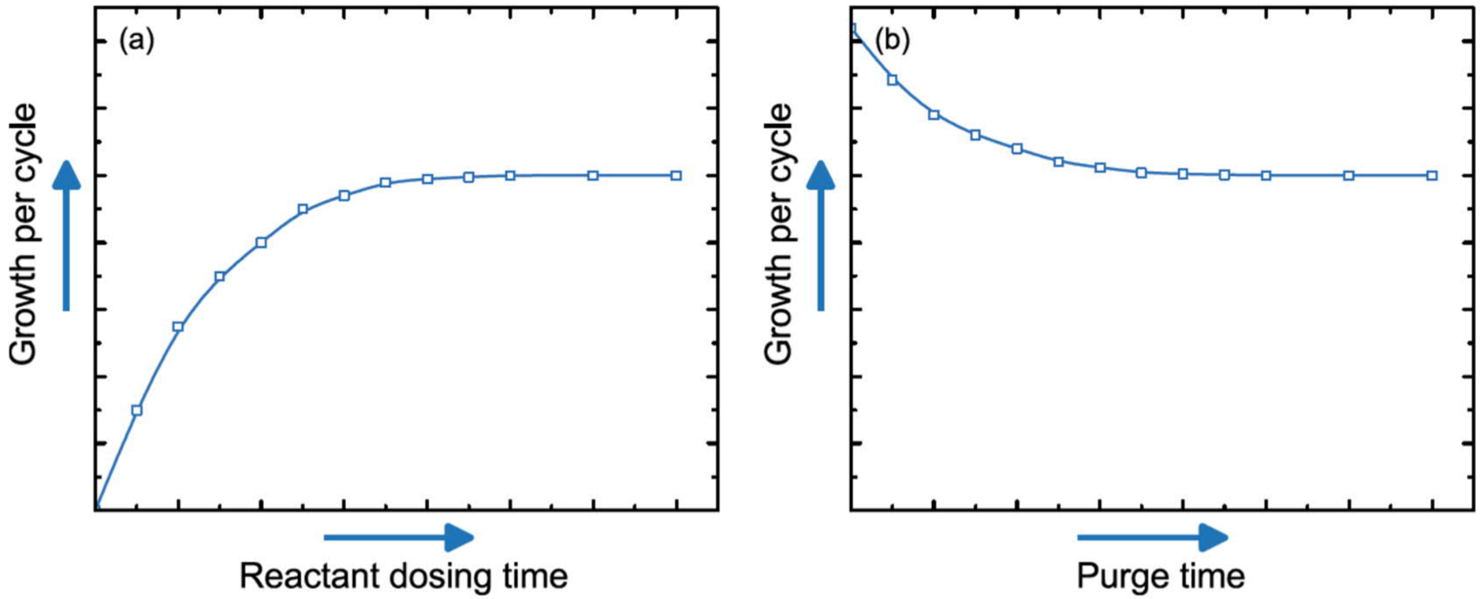


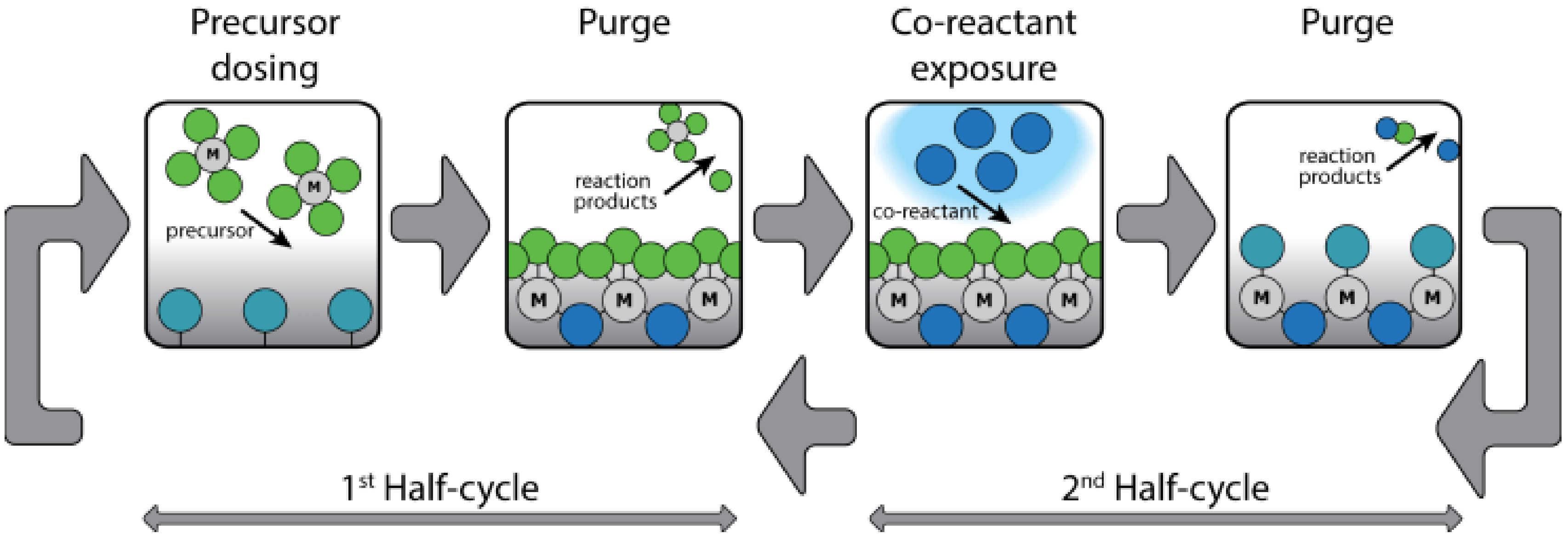
HfO_2-ALD gate oxide
$HfCl_4 + H_2O$

ALD cycle

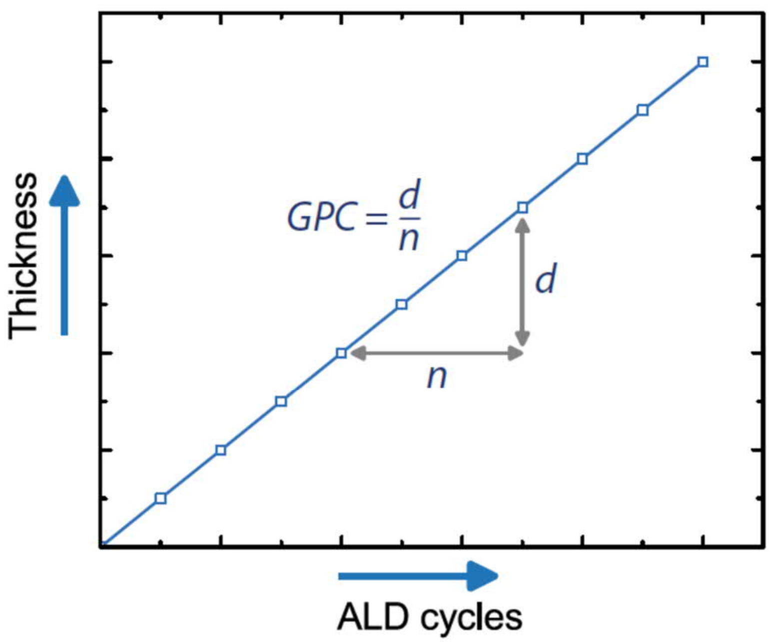


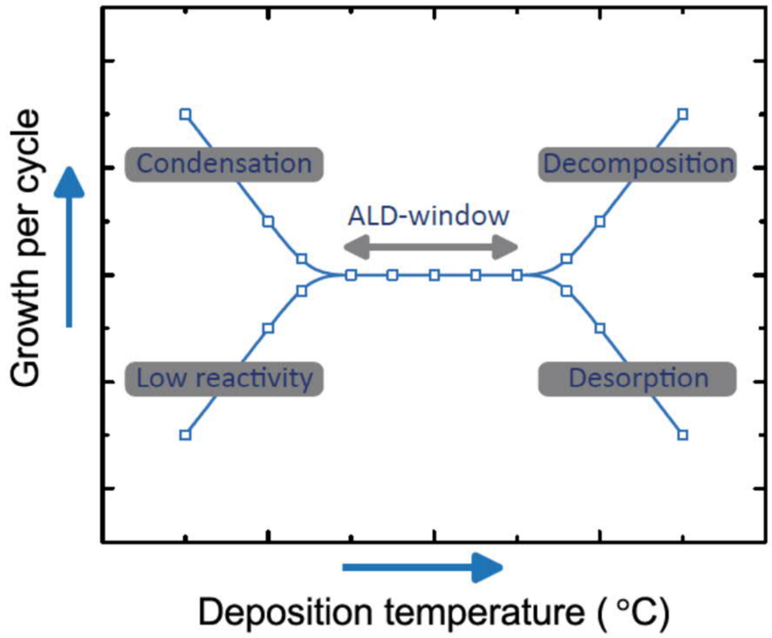


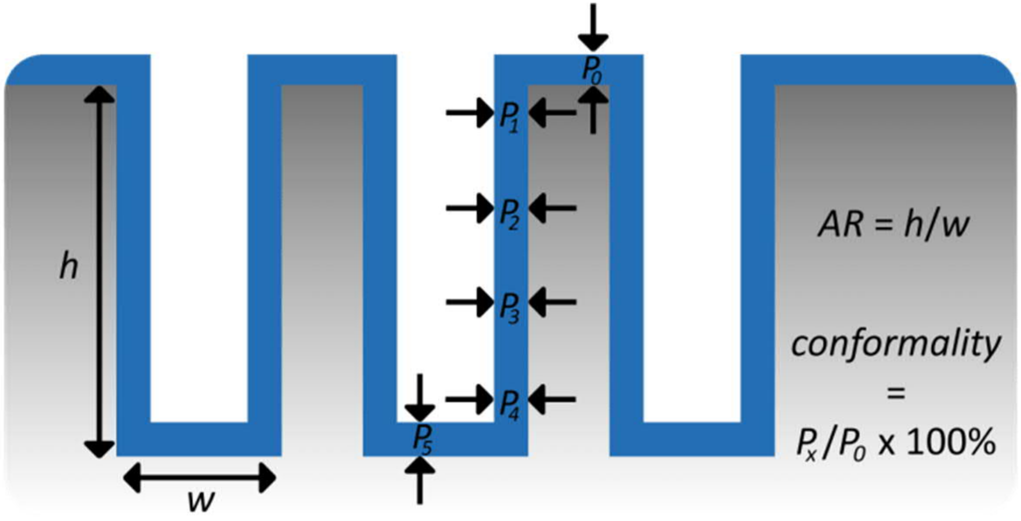




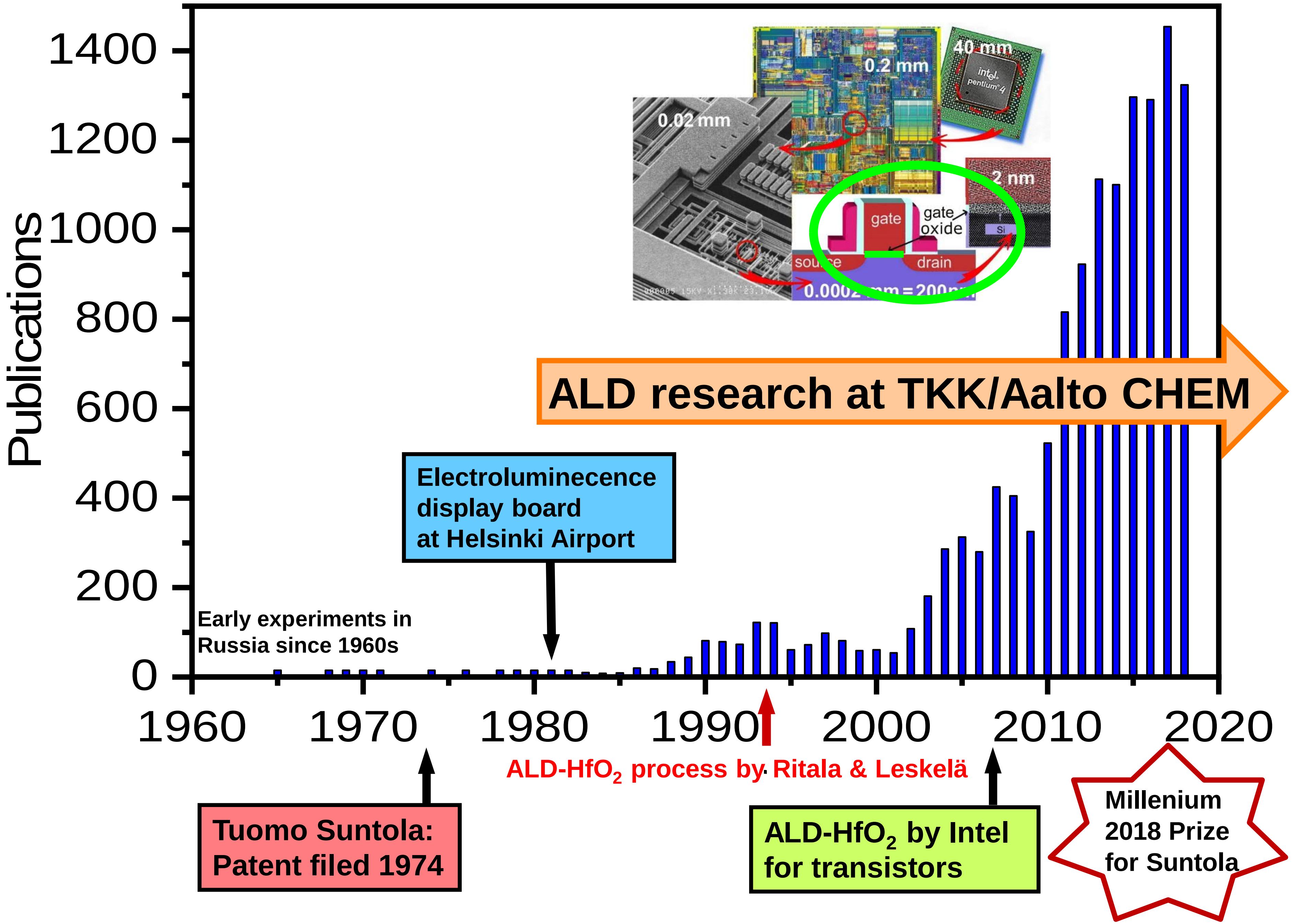
FILM GROWTH RATE: Growth per Cycle (GPC) [Å/cycle]


Thickness
ALD cycles
$GPC = \frac{d}{n}$
d
n


Growth per cycle
Deposition temperature (°C)
Condensation
Decomposition
ALD-window
Low reactivity
Desorption


P_0
P_1
P_2
P_3
P_4
P_5
h
w
$AR = h/w$
conformality
=
P_x/P_0 x 100%

Atomic Layer Deposition (ALD)



Early experiments in Russia since 1960s

Electroluminecence display board at Helsinki Airport

ALD research at TKK/Aalto CHEM

ALD-HfO_2 process by Ritala & Leskelä

Tuomo Suntola: Patent filed 1974

ALD-HfO_2 by Intel for transistors

Millenium 2018 Prize for Suntola

Advantages of ALD

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

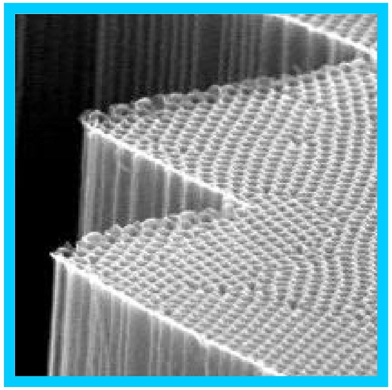
- Excellent conformality

- Low deposition temperature
- Gentle deposition process

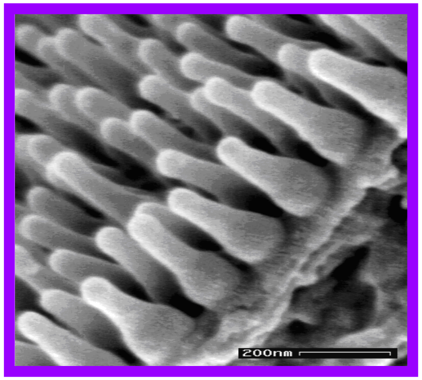
- Organic/polymer films
- Inorganic/organic hybrid materials

ELECTRONICS

NANO

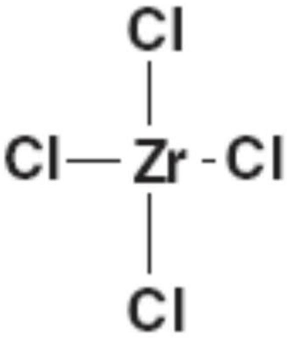


BIO

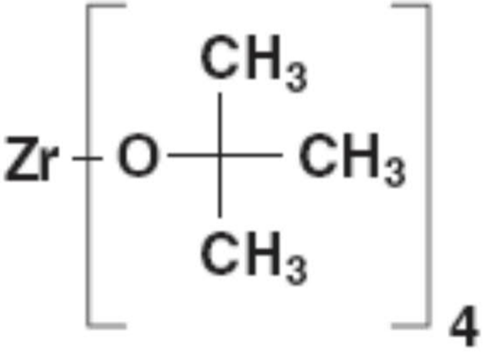


NEW

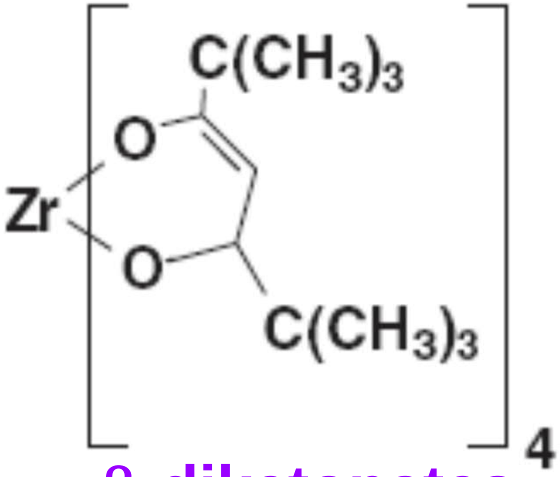
COMMON METAL PRECURSORS in ALD



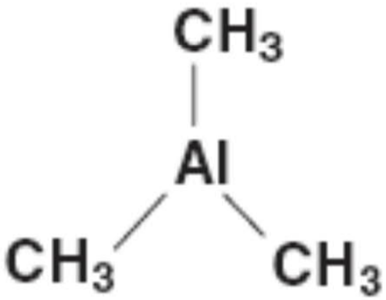
halides

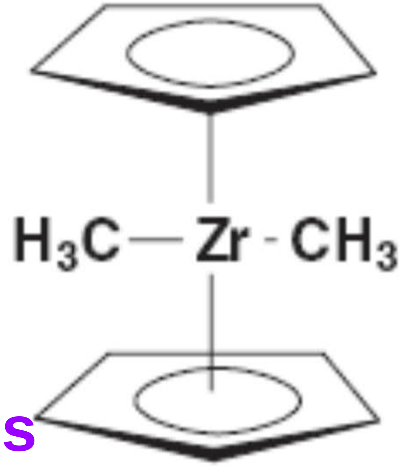


alkoxides



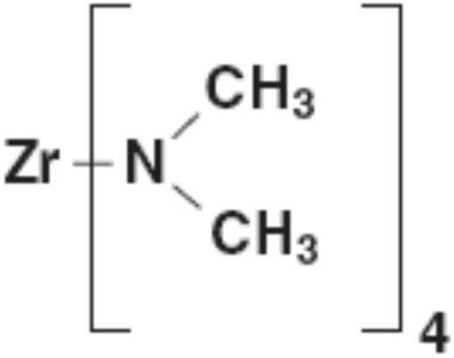
β-diketonates





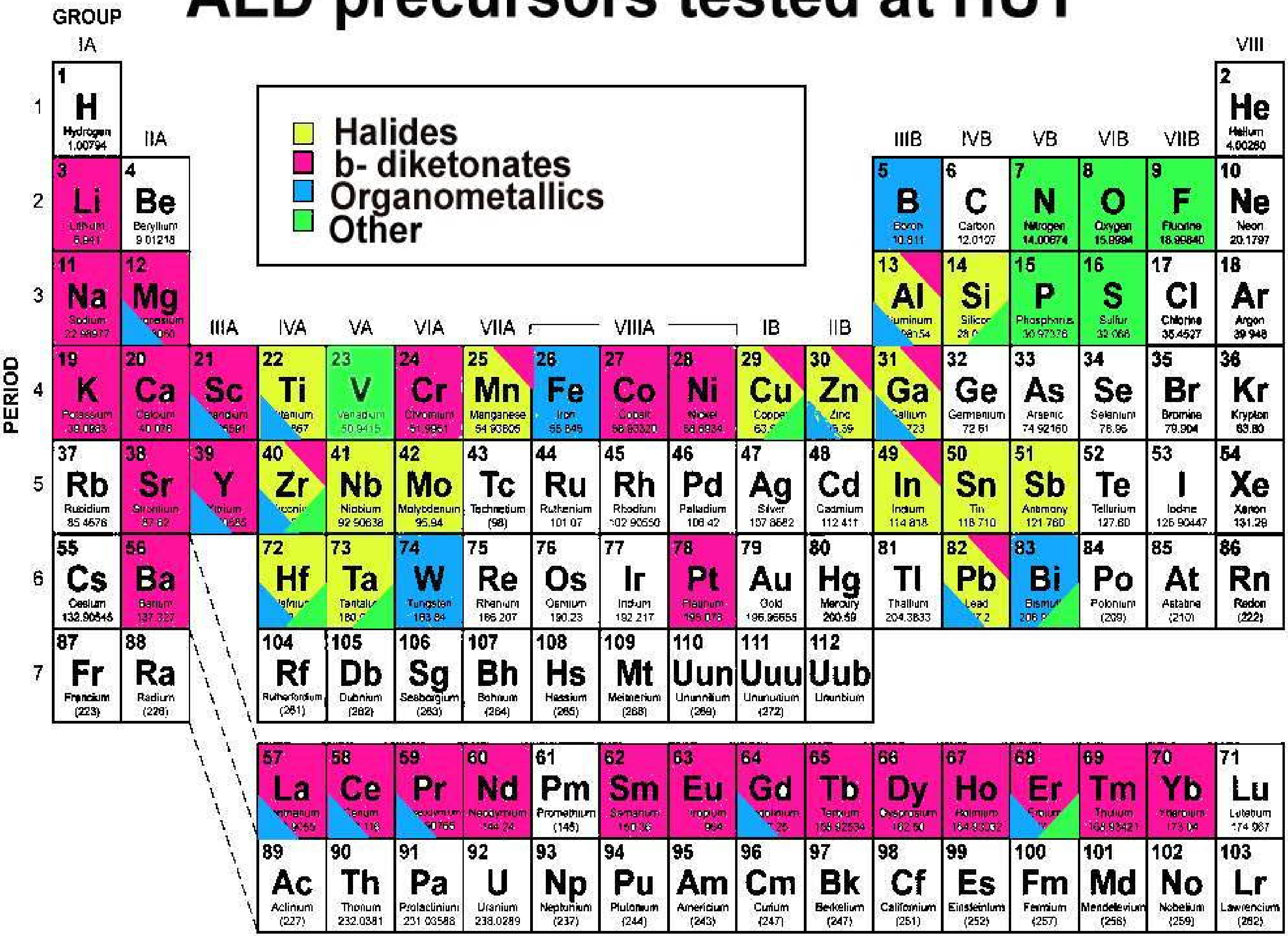
organometallics

e.g. cyclopentadienyls



amido complexes

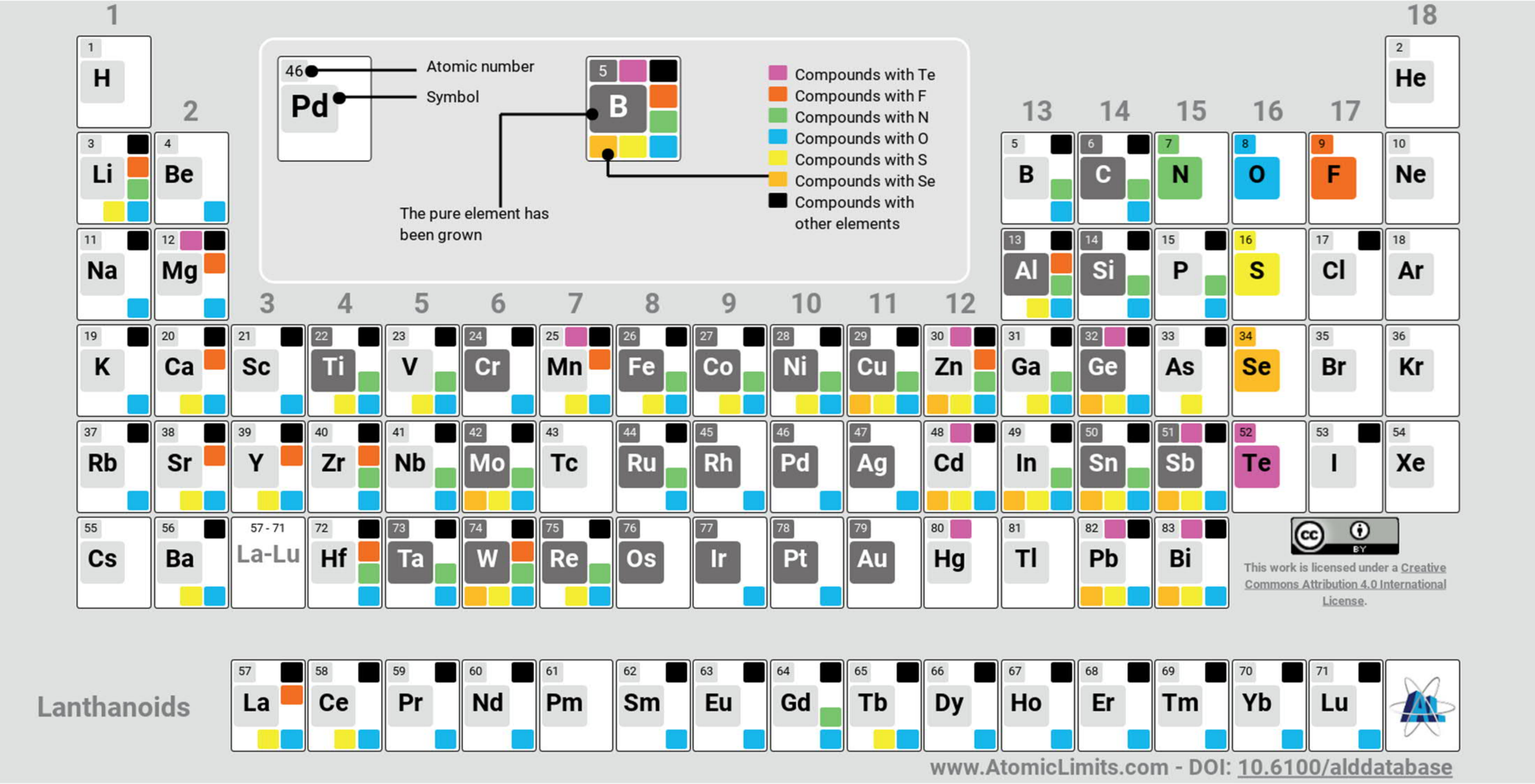
ALD precursors tested at HUT



- 🟨 Halides
- 🟥 b- diketonates
- 🟦 Organometallics
- 🟩 Other

GROUP

PERIOD	IA	IIA	IIIA	IVA	VA	VIA	VIIA	VIIIA			IB	IIB	IIIB	IVB	VB	VIB	VIIB	VIII
1	1 **H** Hydrogen 1.00794																	2 **He** Helium 4.00260
2	3 **Li** Lithium 6.941 🟥	4 **Be** Beryllium 9.01218											5 **B** Boron 10.811 🟦	6 **C** Carbon 12.0107	7 **N** Nitrogen 14.00674 🟩	8 **O** Oxygen 15.9994 🟩	9 **F** Fluorine 18.99840 🟩	10 **Ne** Neon 20.1797
3	11 **Na** Sodium 22.98977 🟥	12 **Mg** gnesium 050 🟥🟦											13 **Al** uminum 98154 🟨🟥🟦	14 **Si** Silicon 28.0 🟨🟩	15 **P** Phosphorus 30.97376 🟩	16 **S** Sulfur 32.066 🟩	17 **Cl** Chlorine 35.4527	18 **Ar** Argon 39.948
4	19 **K** Potassium 39.0983 🟥	20 **Ca** Calcium 40.078 🟥	21 **Sc** andium 5591 🟥🟦	22 **Ti** tanium 867 🟨🟦	23 **V** Vanadium 50.9415 🟩	24 **Cr** Chromium 51.9961 🟥	25 **Mn** Manganese 54.93805 🟨🟥	26 **Fe** Iron 55.845 🟦	27 **Co** Cobalt 58.93320 🟥	28 **Ni** Nickel 58.6934 🟥	29 **Cu** Copper 63.5 🟨🟥🟩	30 **Zn** Zinc 5.39 🟨🟥🟦	31 **Ga** allium 723 🟨🟥🟦	32 **Ge** Germanium 72.61	33 **As** Arsenic 74.92160	34 **Se** Selenium 78.96	35 **Br** Bromine 79.904	36 **Kr** Krypton 83.80
5	37 **Rb** Rubidium 85.4678	38 **Sr** Strontium 87.62 🟥	39 **Y** ttrium 585 🟥🟦	40 **Zr** rconi 🟨🟥🟦🟩	41 **Nb** Niobium 92.90638 🟨	42 **Mo** Molybdenum 95.94 🟨	43 **Tc** Technetium (98)	44 **Ru** Ruthenium 101.07	45 **Rh** Rhodium 102.90550	46 **Pd** Palladium 106.42	47 **Ag** Silver 107.8682	48 **Cd** Cadmium 112.411	49 **In** Indium 114.818 🟨🟥	50 **Sn** Tin 118.710 🟨	51 **Sb** Antimony 121.760 🟨	52 **Te** Tellurium 127.60	53 **I** Iodine 126.90447	54 **Xe** Xenon 131.29
6	55 **Cs** Cesium 132.90545	56 **Ba** Barium 137.327 🟥		72 **Hf** afniu 🟨🟦🟩	73 **Ta** Tantalu 180. 🟨🟩	74 **W** Tungsten 183.84 🟦	75 **Re** Rhenium 186.207	76 **Os** Osmium 190.23	77 **Ir** Iridium 192.217	78 **Pt** Platinum 195.078 🟥	79 **Au** Gold 196.96655	80 **Hg** Mercury 200.59	81 **Tl** Thallium 204.3833	82 **Pb** Lead 7.2 🟨🟥🟦	83 **Bi** Bismu 208 🟦🟩	84 **Po** Polonium (209)	85 **At** Astatine (210)	86 **Rn** Radon (222)
7	87 **Fr** Francium (223)	88 **Ra** Radium (226)		104 **Rf** Rutherfordium (261)	105 **Db** Dubnium (262)	106 **Sg** Seaborgium (263)	107 **Bh** Bohrium (264)	108 **Hs** Hassium (265)	109 **Mt** Meitnerium (268)	110 **Uun** Ununnilium (269)	111 **Uuu** Unununium (272)	112 **Uub** Ununbium						
				57 **La** nthanum 8.9055 🟥🟦	58 **Ce** erium 116 🟥🟦	59 **Pr** eodymium 90765 🟥🟦	60 **Nd** Neodymium 144.24 🟥	61 **Pm** Promethium (145)	62 **Sm** Samarium 150.36 🟥	63 **Eu** ropium 964 🟥	64 **Gd** dolinium 7.25 🟥🟦	65 **Tb** Terbium 158.92534 🟥	66 **Dy** Dysprosium 162.50 🟥	67 **Ho** Holmium 164.93032 🟥	68 **Er** rbium 🟥🟦🟩	69 **Tm** Thulium 168.93421 🟥	70 **Yb** Ytterbium 173.04 🟥	71 **Lu** Lutetium 174.967
				89 **Ac** Actinium (227)	90 **Th** Thorium 232.0381	91 **Pa** Protactinium 231.03588	92 **U** Uranium 238.0289	93 **Np** Neptunium (237)	94 **Pu** Plutonium (244)	95 **Am** Americium (243)	96 **Cm** Curium (247)	97 **Bk** Berkelium (247)	98 **Cf** Californium (251)	99 **Es** Einsteinium (252)	100 **Fm** Fermium (257)	101 **Md** Mendelevium (258)	102 **No** Nobelium (259)	103 **Lr** Lawrencium (262)



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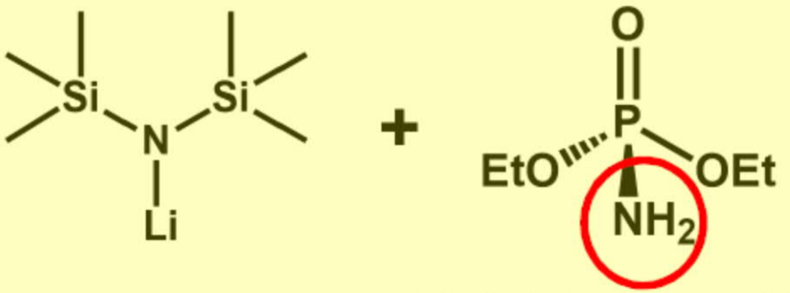
mons.wikimedia.org/w/index.php?curid=78838925

COMMON CO-REACTANTS (second precursor) in ALD

- 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

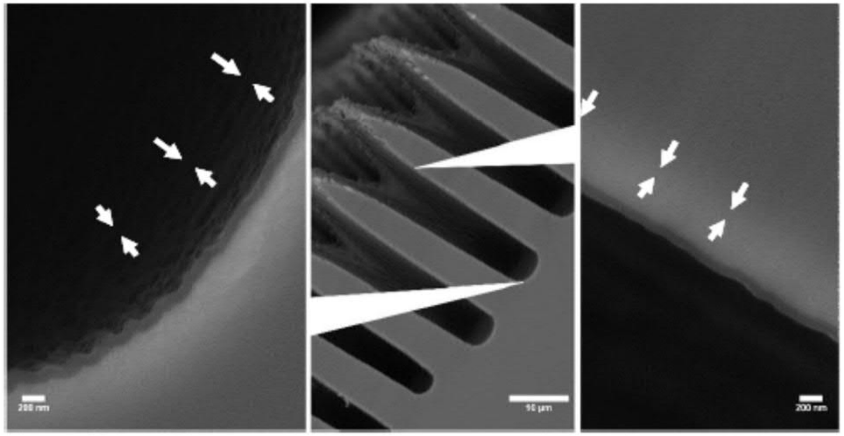
LiPON BY ALD WITH TOYOTA

- Lithium phosphorous oxynitride $Li_xPO_yN_z$
- A promising solid-state electrolyte for thin-film Li-ion microbattery

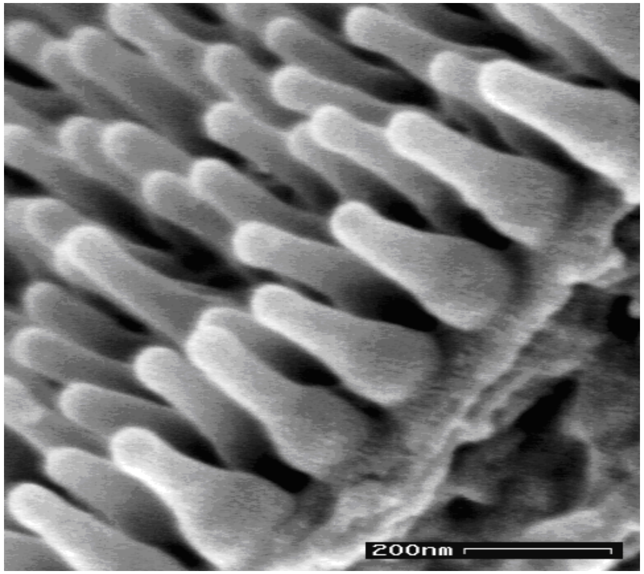


Diethyl phosphoramidate

RBS-NRA	Ionic cond.
$Li_{0.94}PO_{3.00}N_{0.60}$	7×10^{-7} S cm^{-1}



M. Nisula, Y. Shindo, H. Koga & M. Karppinen, *Chem. Mater.* **27**, 6987 (2015).



CICADA WING

- **Peculiar surface-nanostructure**

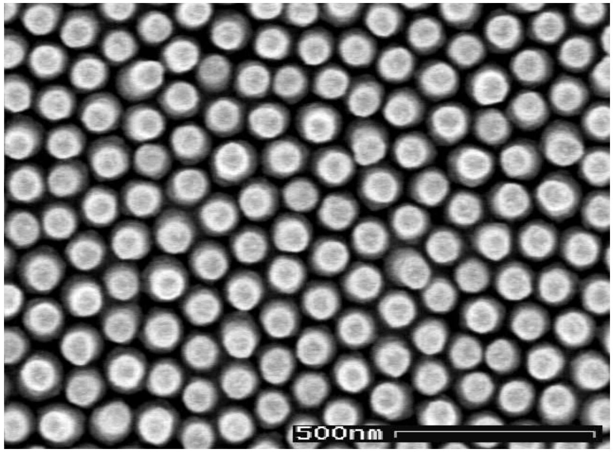
  200-nm high nanopillars with a WAXY SURFACE
- **superhydrofobic**

ZnO

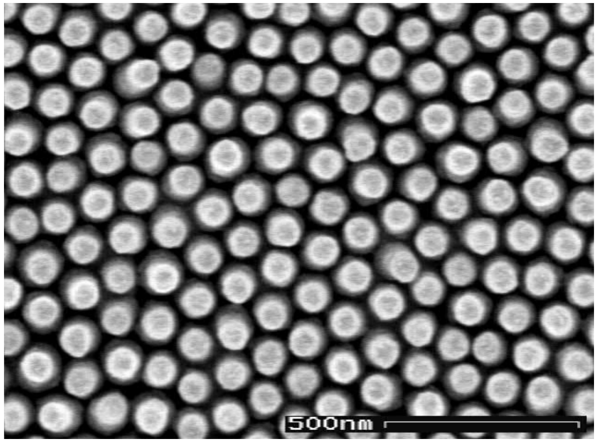
- **Reversible change from hydrofobic to hydrophilic upon UV-radiation**

CICADA WING + ZnO (+ few-nm Al_2O_3)

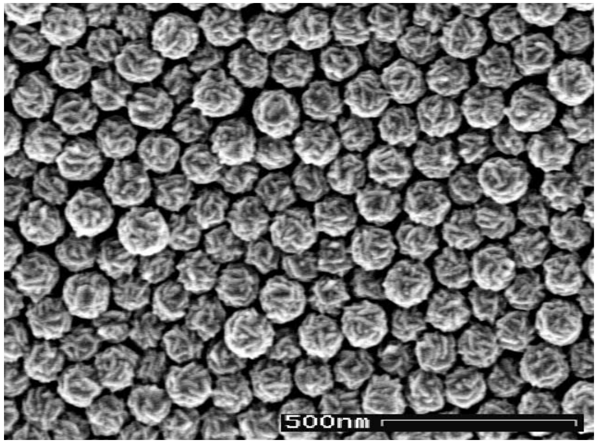
- **Conformal coating of the wing by a thin layer of ZnO (~20 nm) by means of ALD**
- **Reversible change from superhydrofobic to superhydrophilic upon UV-radiation**



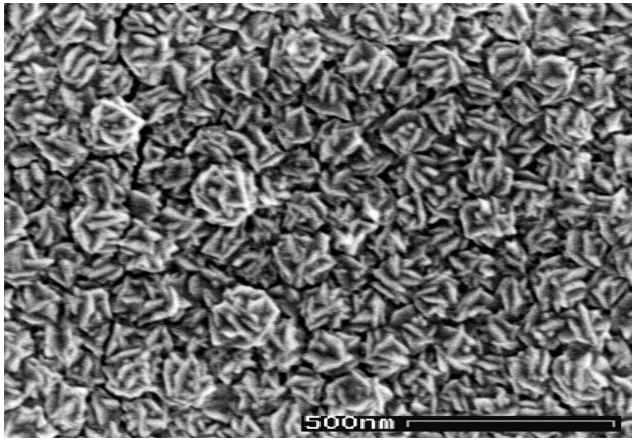
J. Malm, E. Sahramo, M. Karppinen & R. Ras, *Chem. Mater.* **22**, 3349 (2010).



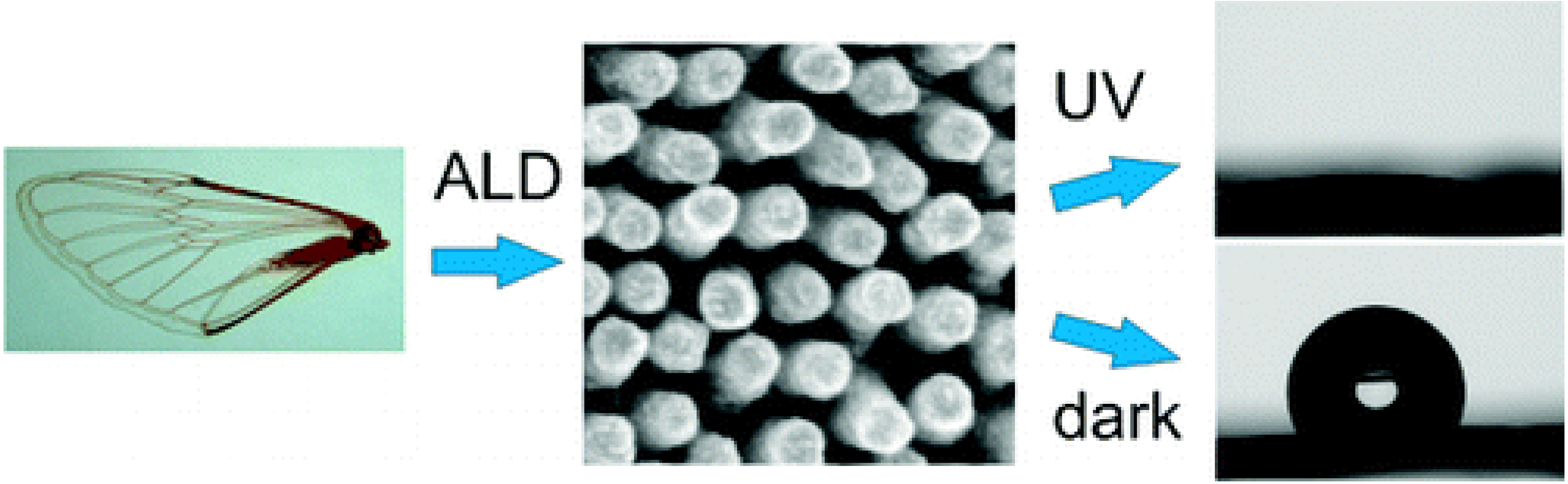
100 cycles (20 nm)



300 cycles (60 nm)

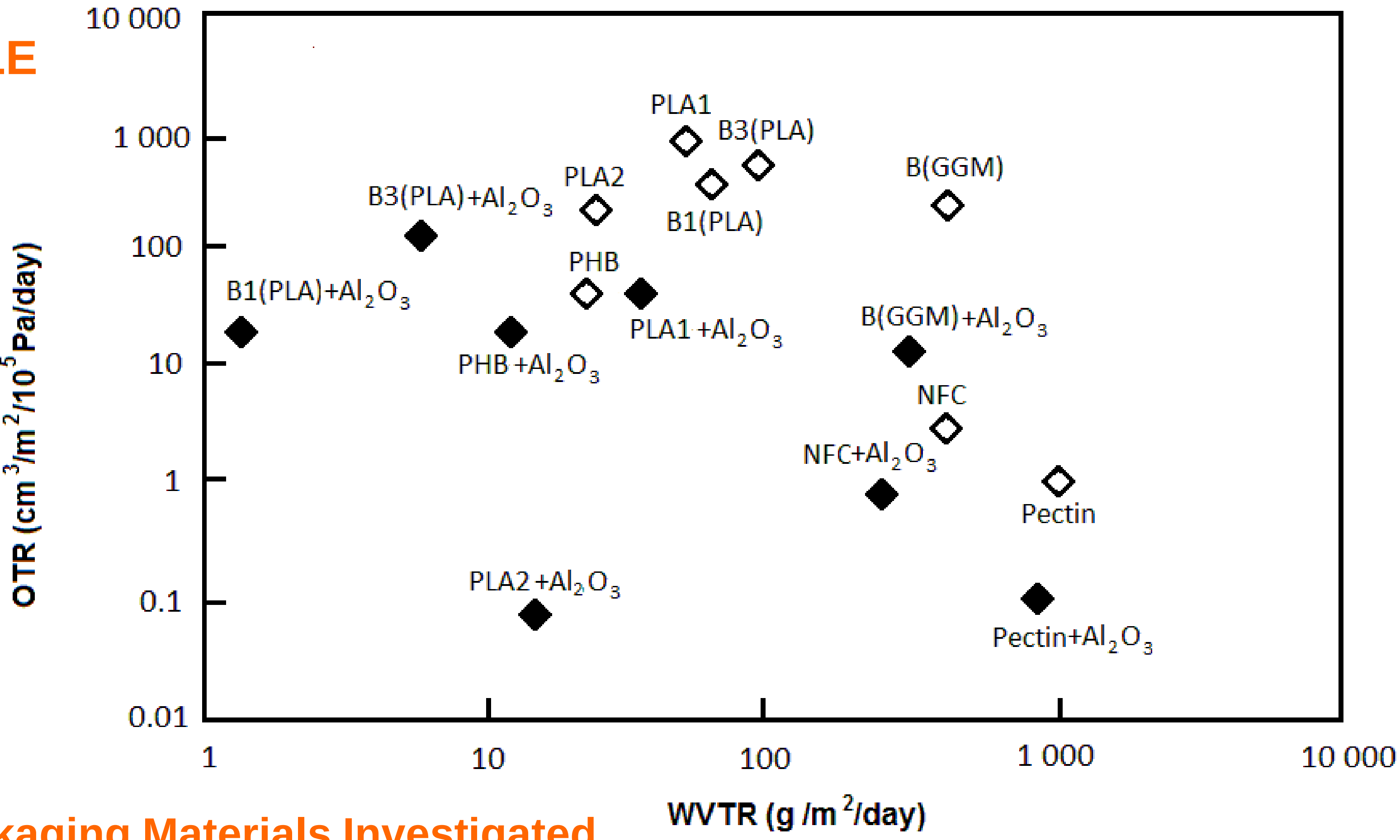


500 cycles (100 nm)



RECYCLABLE BIO-BASED PACKAGING MATERIALS

Problem: Bad gas-barriers



O_2- and H_2O-vapour transmission

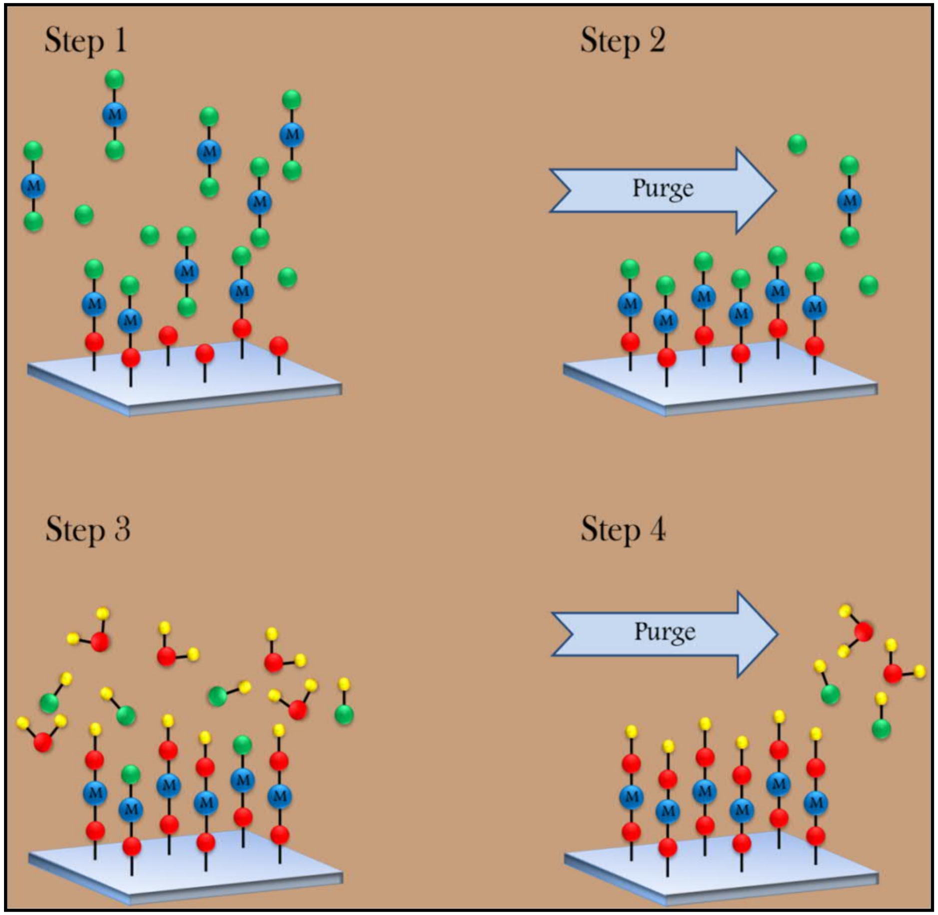
◇ **Biopolymer**

◆ **Biopolymer + 25 nm ALD-Al_2O_3**

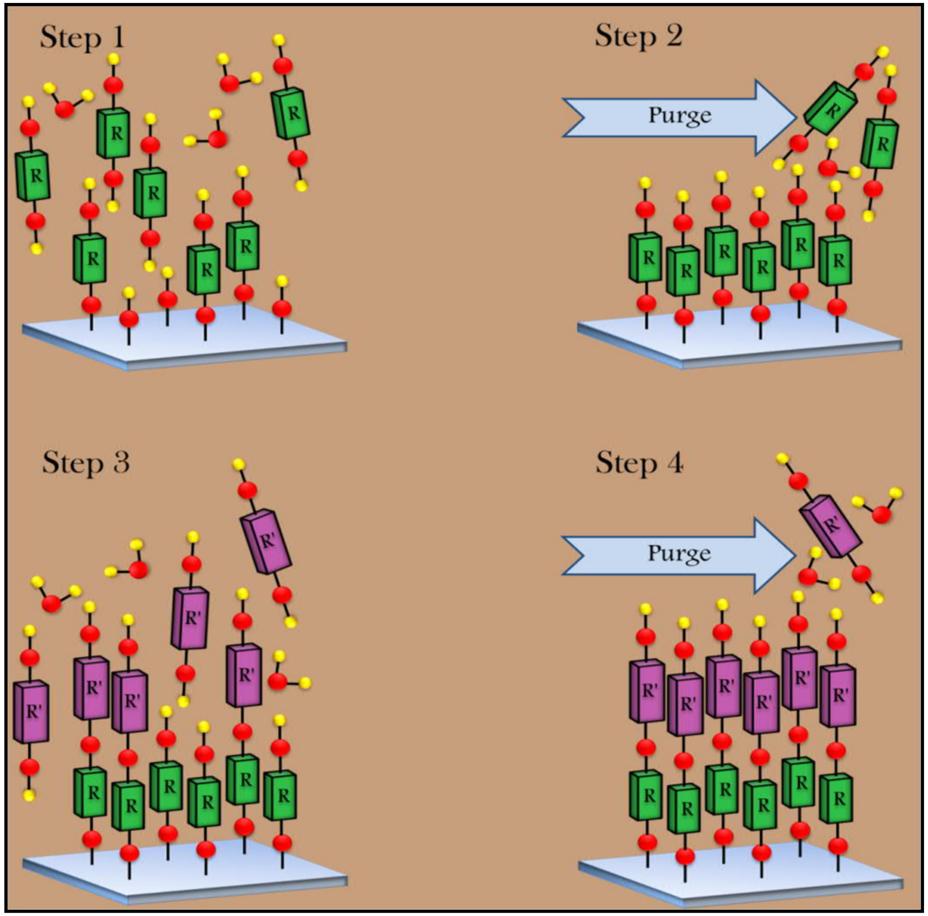
Bio-based Packaging Materials Investigated

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**

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



ALD (Atomic Layer Deposition)

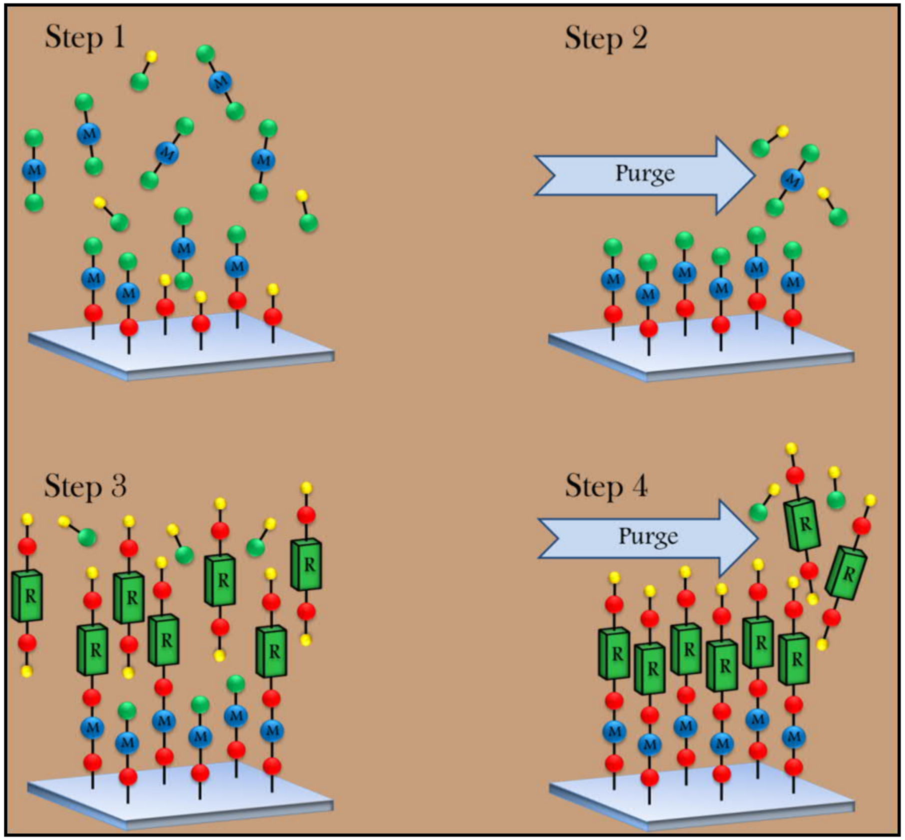


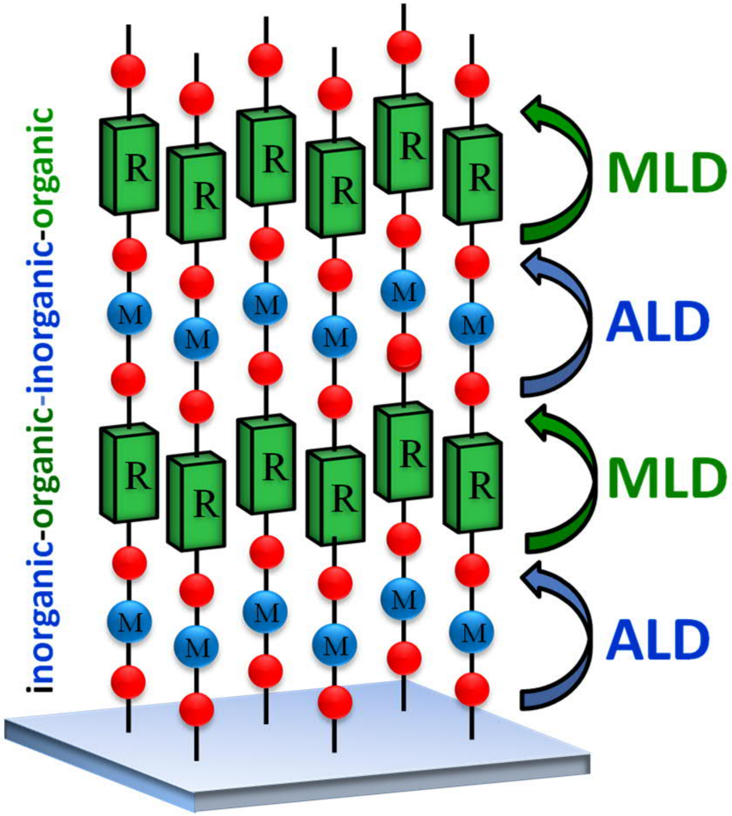
MLD (Molecular Layer Deposition)

High-quality INORGANIC thin films with atomic level control

ORGANICS !

Inorganic-Organic (Metal-Organic) Hybrid Thin Films by Combined ALD/MLD

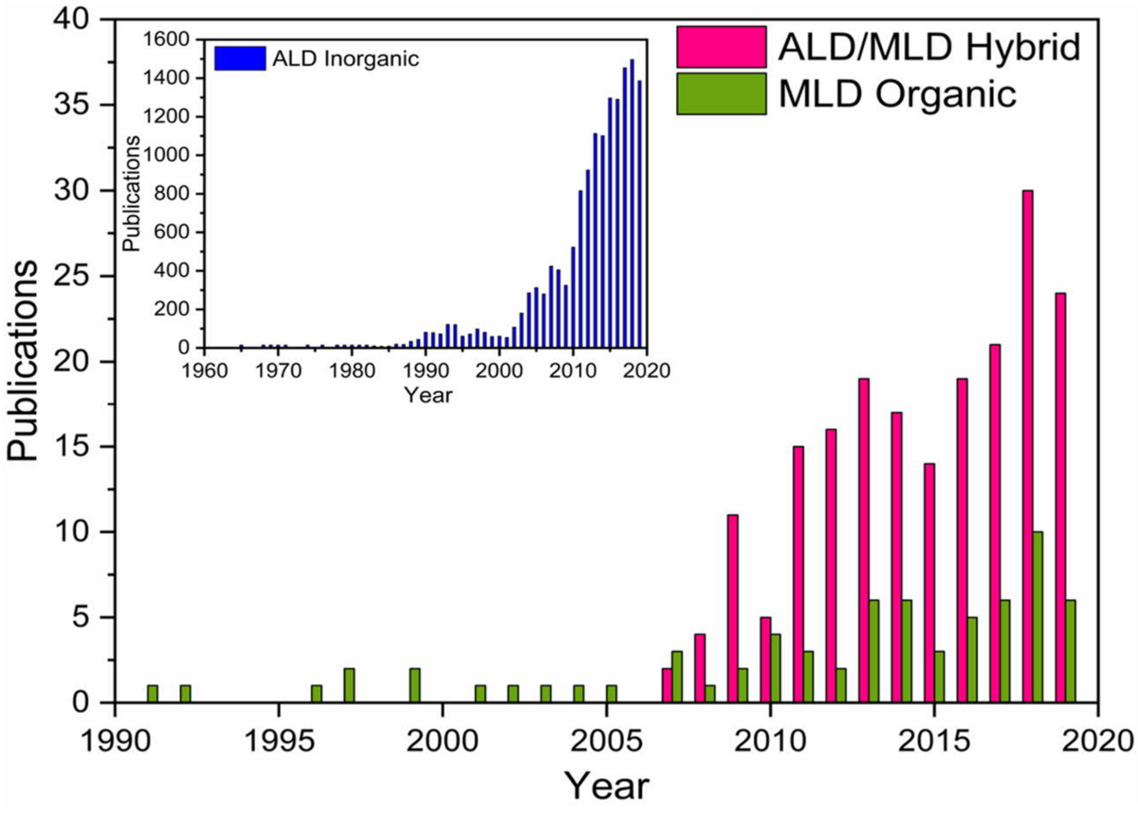




FLEXIBLE MULTIFUNCTIONAL SINGLE-PHASE HYBRID MATERIALS !!!

ANNUALLY PUBLISHED PAPERS:

MLD & ALD/MLD



Yoshimura, Tatsuura & Sotoyama, *Appl. Phys. Lett.* **1991,** *59,* 482.

Yoshimura, Tatsuura, Sotoyama, Matsuura & Hayano, *Appl. Phys. Lett.* **1992,** *60,* 268.

Kubono, Yuasa, Shao, Umemoto & Okui, *Thin Solid Films* **1996,** *289,* 107.

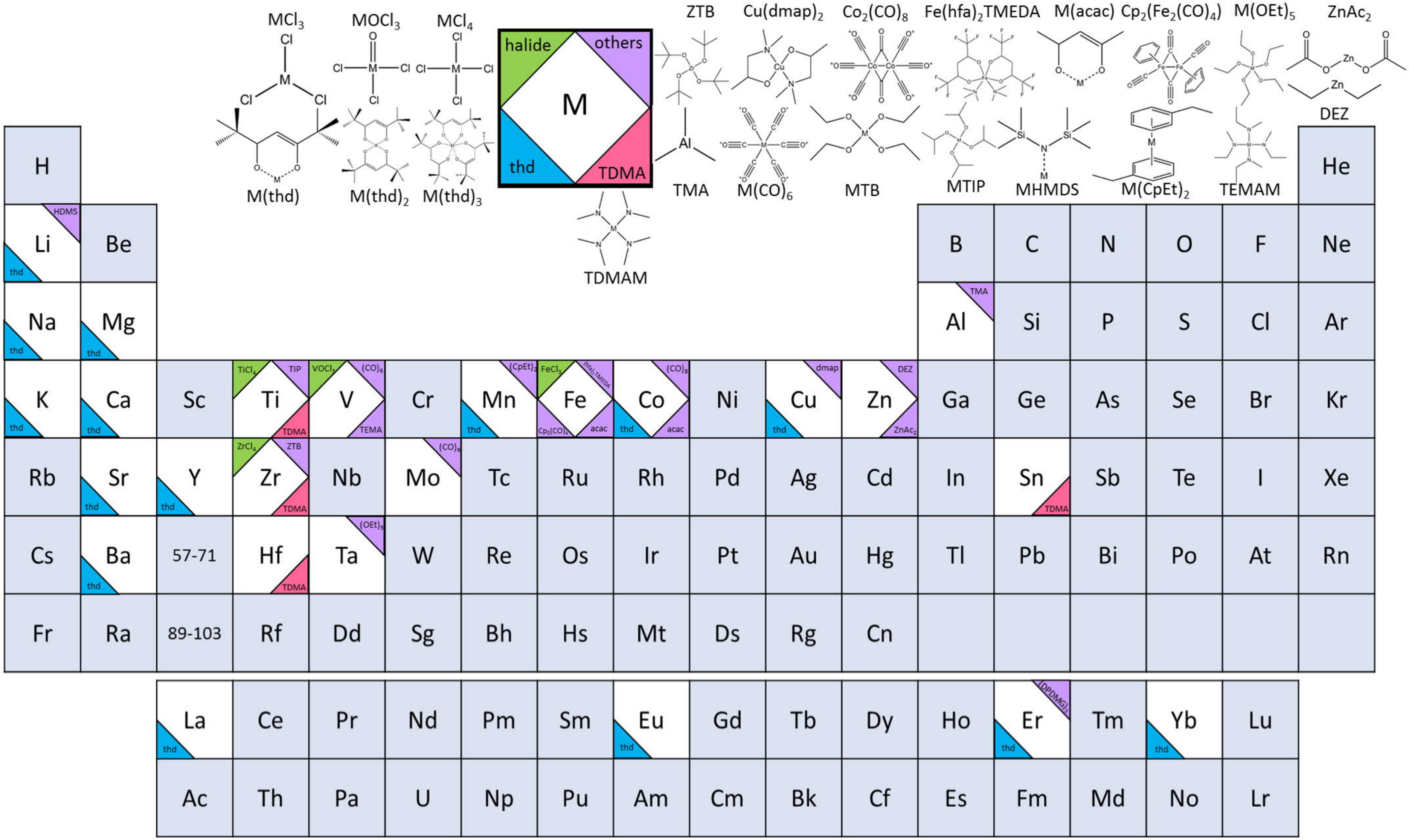
Shao, Umemoto, Kikutani & Okui, *Polymer* **1997,** *38,* 459.

Lee, Ryu, Choi, Lee, Im & Sung, *J. Am. Chem. Soc.* **2007,** *129,* 16034.

Smirnov, Zemtsova, Belikov, Zheldakov, Morozov, Polyachonok & Aleskovskii, *Dokl. Phys. Chem.* **2007,** *413,* 95.

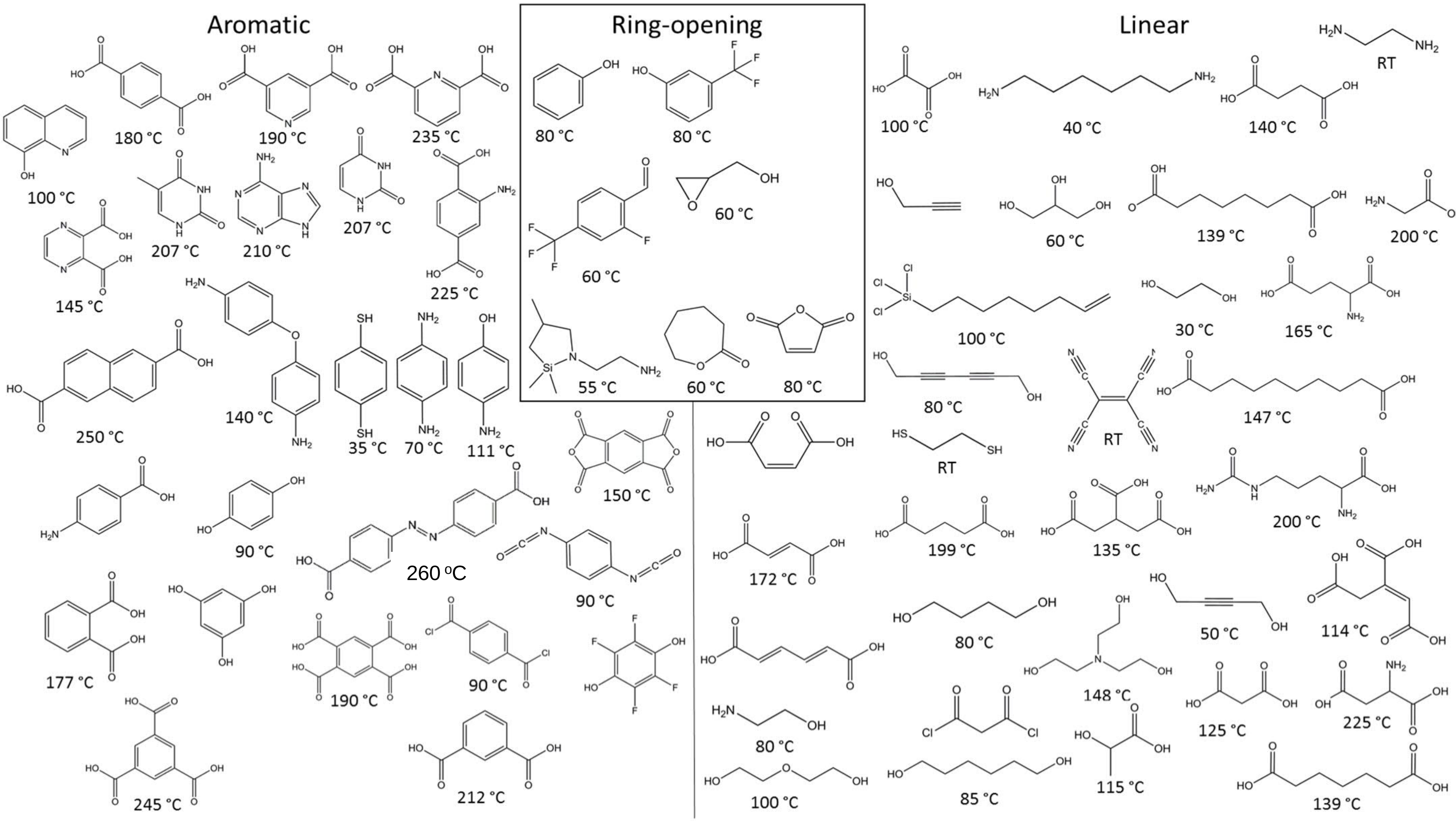
Nilsen, Klepper, Nielsen & Fjellvåg, *ECS Trans.* **2008,** *16,* 3.

Dameron, Seghete, Burton, Davidson, Cavanagh, Bertrand & George, *Chem. Mater.* **2008,** *20,* 3315.



Aalto University
School of Chemical
Technology

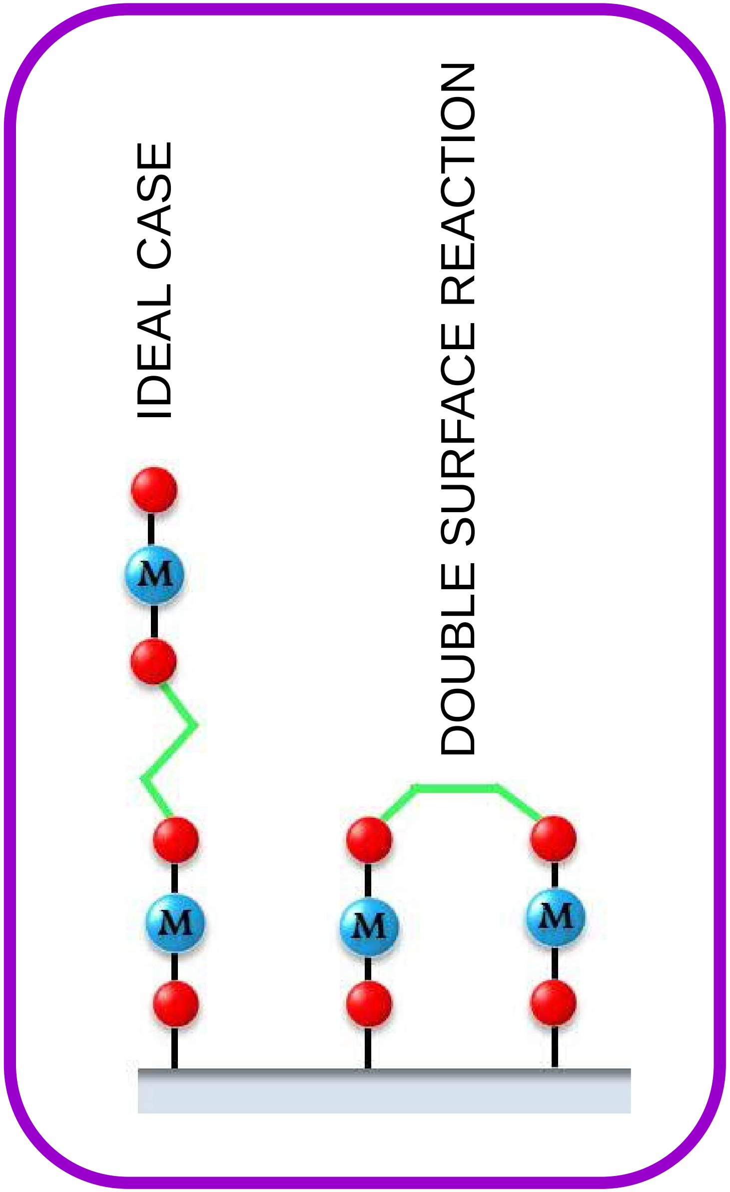
ALD/MLD Processes: Metal Precursors



Aalto University
School of Chemical
Technology

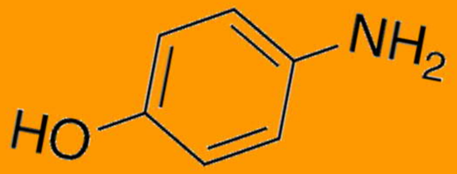
ALD/MLD Processes: Organic Precursors

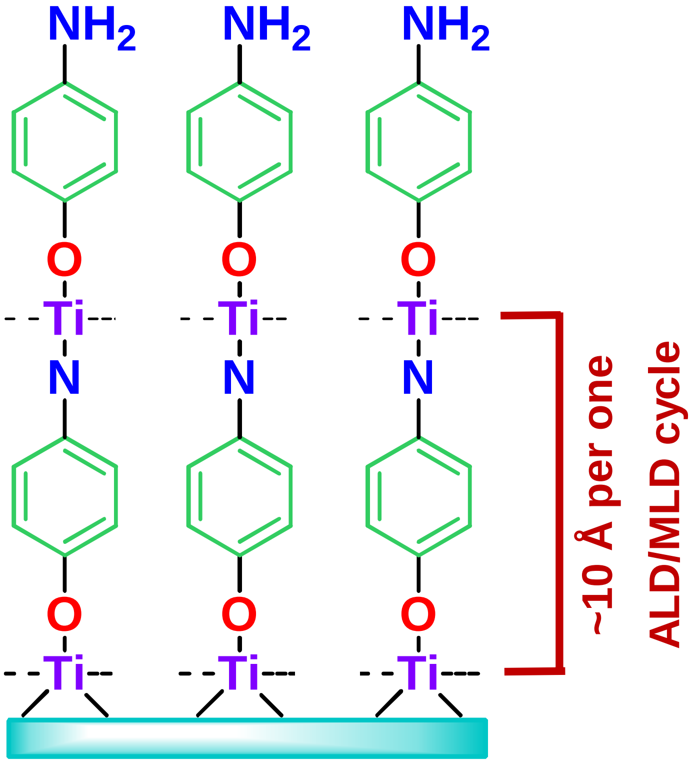
(sublimation temperatures !)



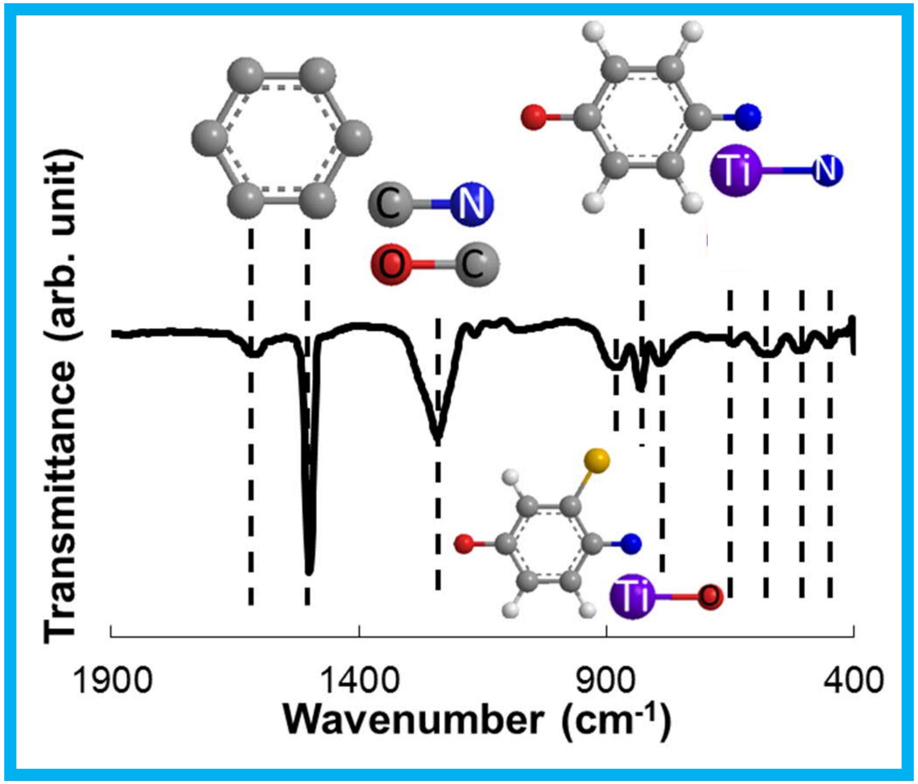
P. Sundberg & M. Karppinen,
Organic and inorganic-organic thin film structures by molecular layer deposition:
A review, *Beilstein Journal of Nanotechnology* **5**, 1104 (2014).

$TiCl_4$ + Aminophenol





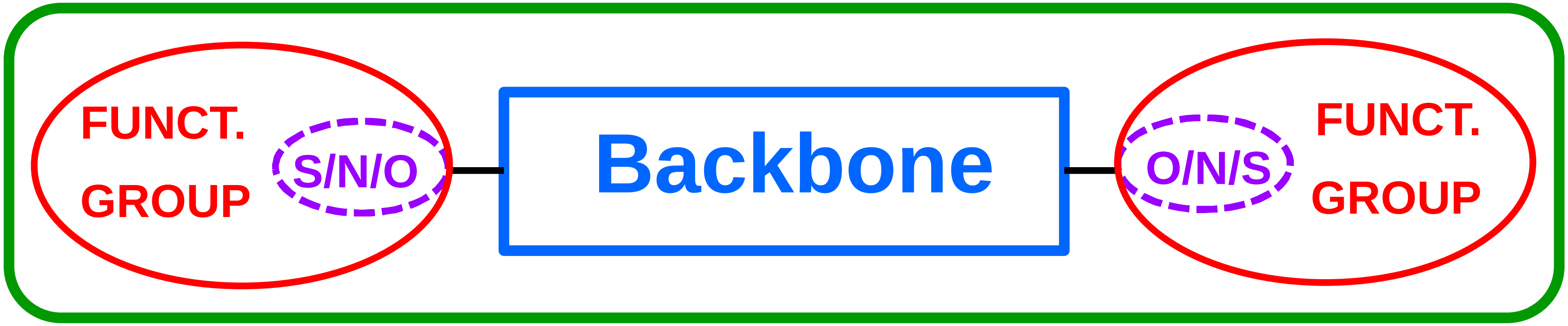
FTIR



Aalto University
School of Chemical Technology

P. Sundberg & M. Karppinen,
Organic-inorganic thin films from $TiCl_4$ and 4-aminophenol precursors: A model case of ALD/MLD hybrid-material growth?,
Eur. J. Inorg. Chem. **2014**, 968 (2014).

- **Reactivity** of the **functional groups** towards the metal precursor
- **Bonding site (e.g. O, N or S) → M-O / M-S / M-S bond in the hybrid**
- **Backbone**: size, chemistry, functionality → **Remains in the hybrid !!!**



EXAMPLES

ALD: H – O – H

HO – CH_2-CH_2 – OH

HO – benzene – OH

ALD: NH_3

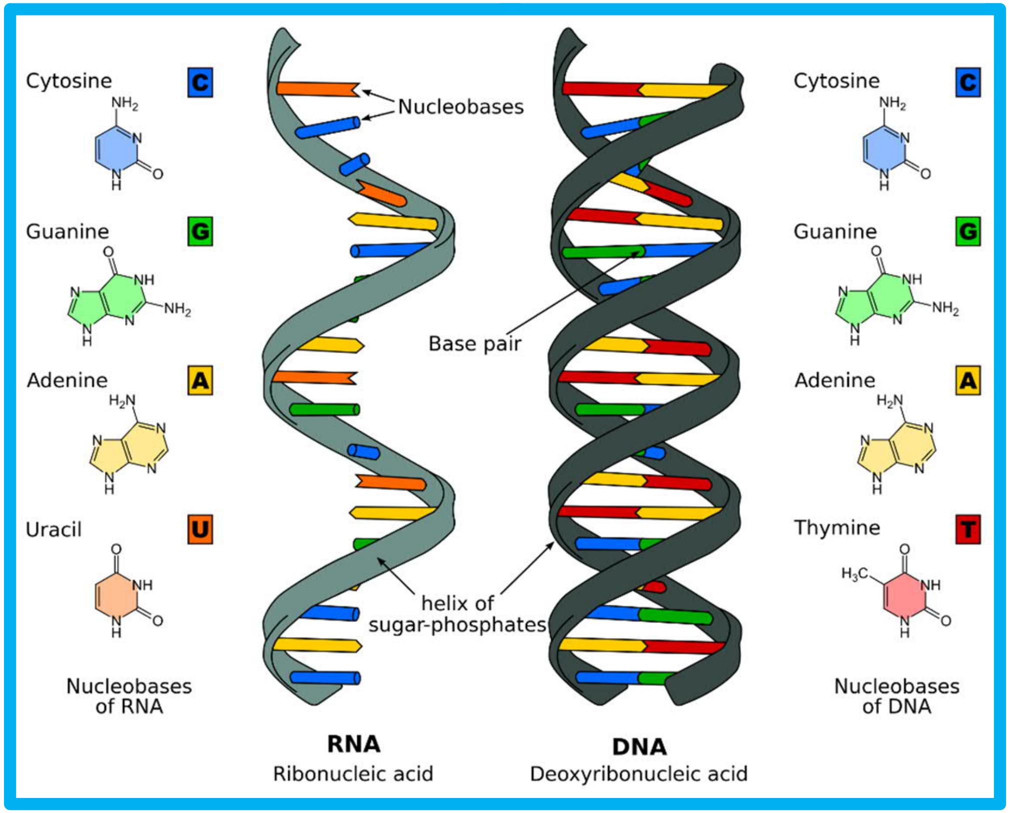
H_2N – backbone – NH_2

ALD: O_3

HOOC – backbone – COOH

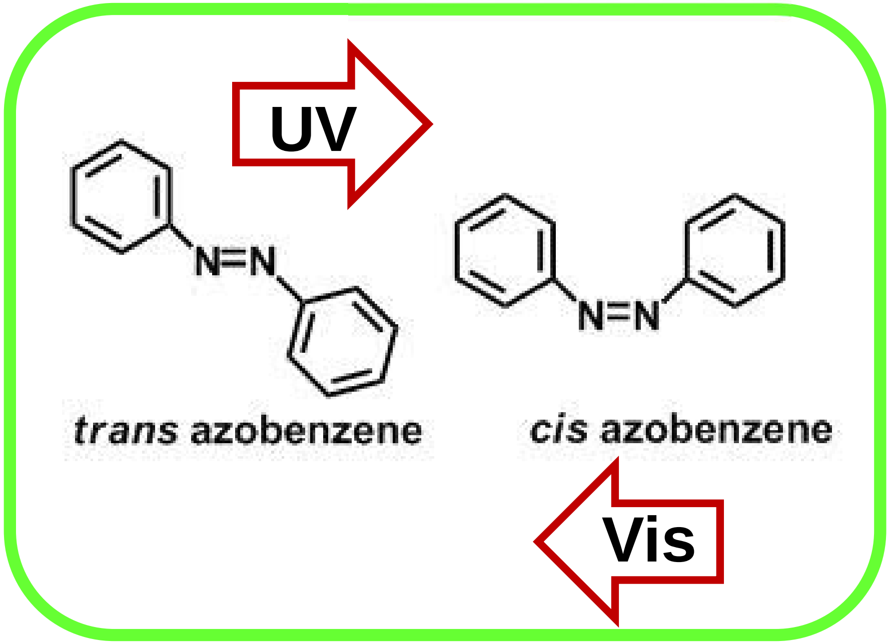
ORGANIC PRECURSOR

NUCLEOBASES FROM NATURE



Z. Giedraityte, O. Lopez-Acevedo, L.A. Espinosa Leal,
V. Pale, J. Sainio, T.S. Tripathi & M. Karppinen,
J. Phys. Chem. C **120**, 26342 (2016).

PHOTORESPONSIVE AZOBENZENE

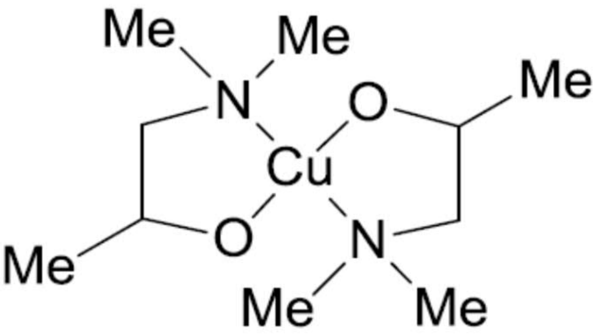


A. Khayyami & M. Karppinen, *Chem. Mater.* 30, 5904 (2018).

A. Khayyami, A. Philip & M. Karppinen,
Angew. Chem. Int. Ed. 58, 13400 (2019).

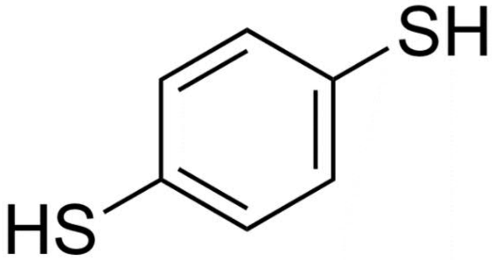
Aalto University
School of Chemical
Engineering

NEW EXCITING ORGANIC COMPONENTS



Cu(dmap)$_2$

T_{subl} = 60 °C
7 s / 5 s N_2



Benzene-1,4-dithiol)

T_{subl} = 35 °C
10 s / 10 s N_2

Low-temperature ALD/MLD

T_{dep} = 80 – 140 °C

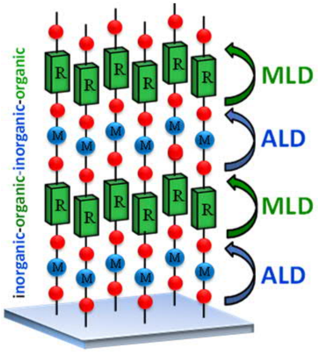
GPC = 1.9 – 0.8 Å/cycle

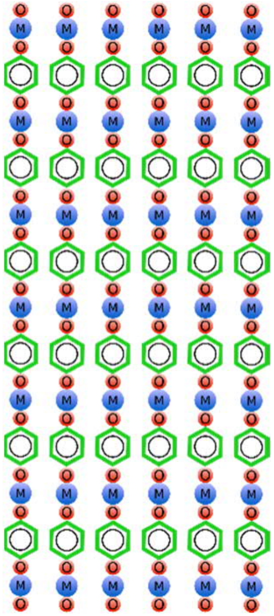
D.J. Hagen, L. Mai, A. Devi, J. Sainio & M. Karppinen,
Atomic/molecular layer deposition of Cu-organic thin films,
Dalton Transactions **47**, 15791 (2018).

⬡ **Organic** (e.g. benzene)

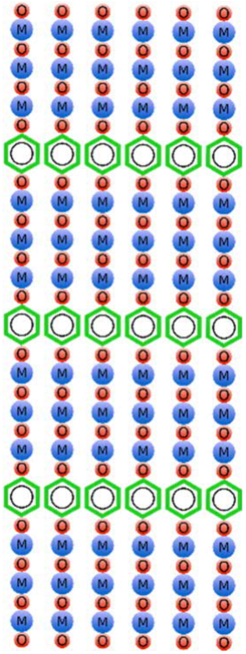
M **Metal**

O **Oxygen** (or N, S, …)

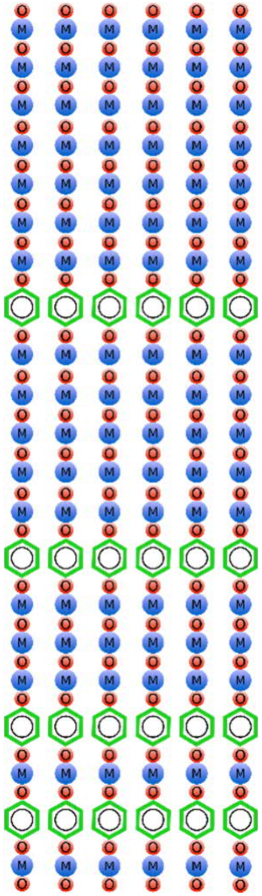




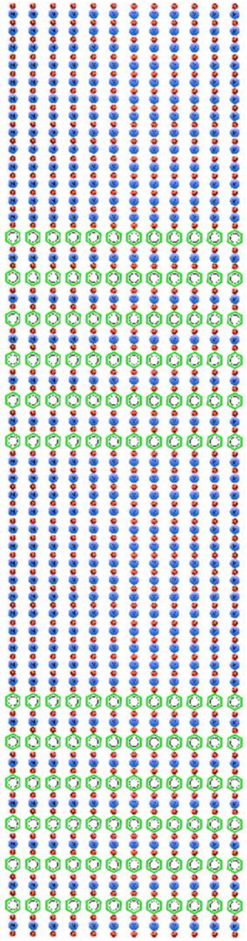
Simple Metal-Organic Network (amorphous or crystalline)



Superlattice



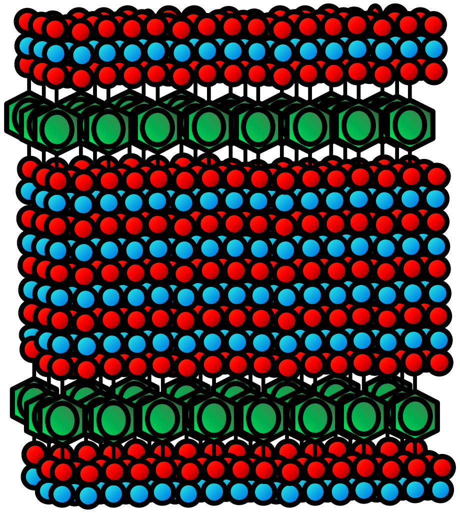
Gradient hybrid

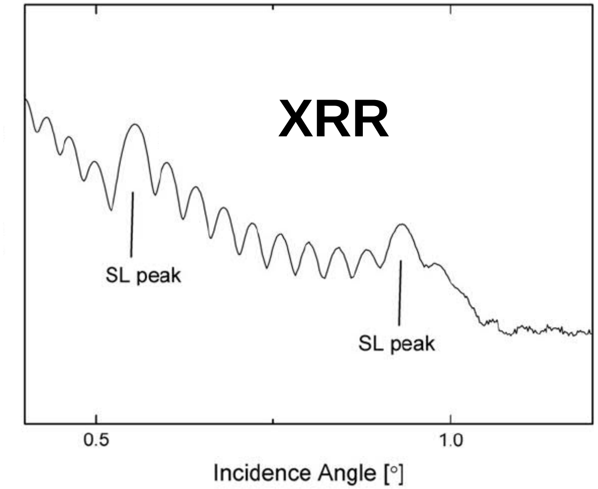


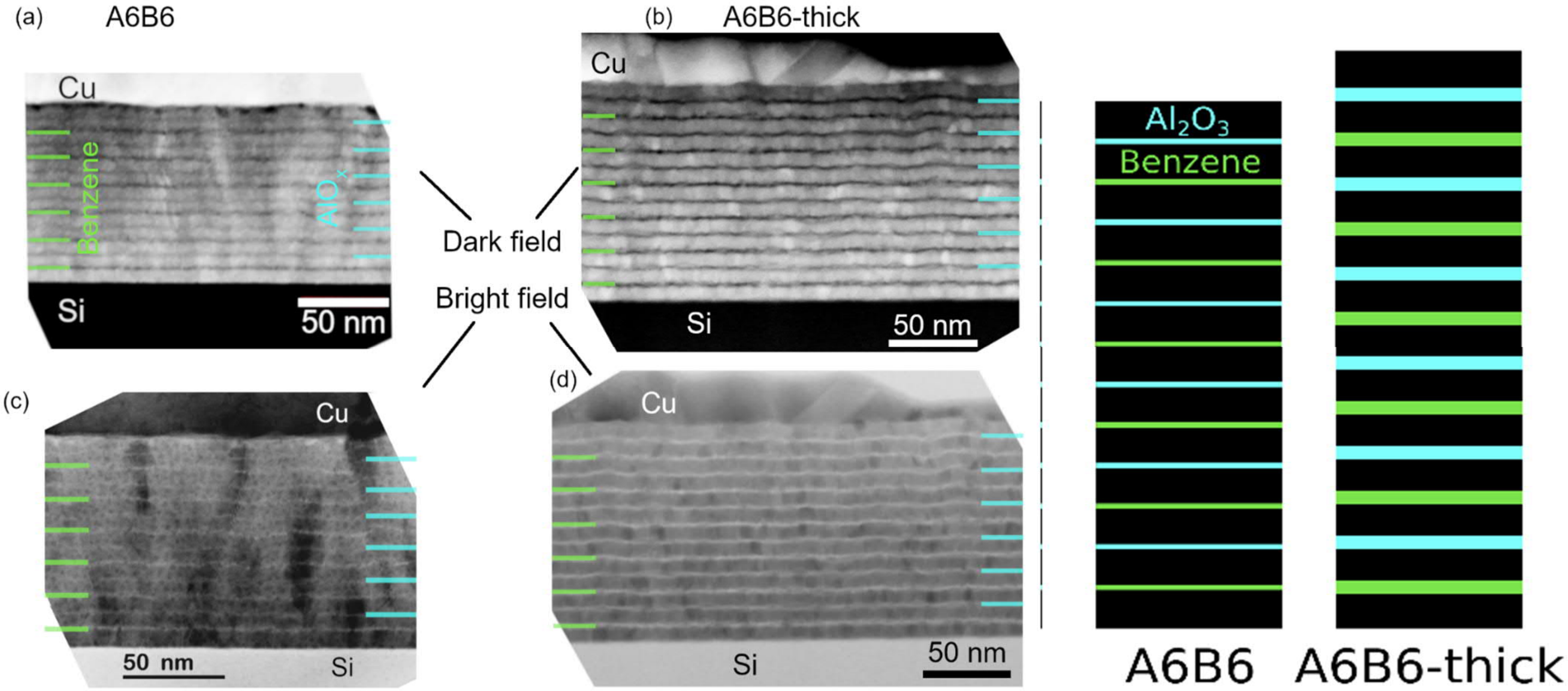
Nanolaminate

DIFFERENT LAYER SEQUENCES BY DESIGN

ZnO:benzene
SUPERLATTICE







POSSIBLE APPLICATIONS OF ALD/MLD FILMS …

- **GAS-BARRIER COATINGS**

  Al_2O_3 + hybrid Al-organic nanolaminate coatings on biopolymers:
  → **Enhanced mechanical & thereby oxygen-gas barrier properties**

- **UV- and IR-to-Vis Conversion Layers for SOLAR CELLS**

  Ln-organic (Ln = e.g. Eu, Yb, Er) films with UV or IR-absorbing organics
  → **More efficient utilization of solar radiation**

- **FLEXIBLE Li-ORGANIC MICROBATTERY**

  Not-previously-existing Li-organic electrode materials
  → **First all-organic Li-ion microbattery**

- **TEXTILE-INTEGRATED THERMOELECTRICS**

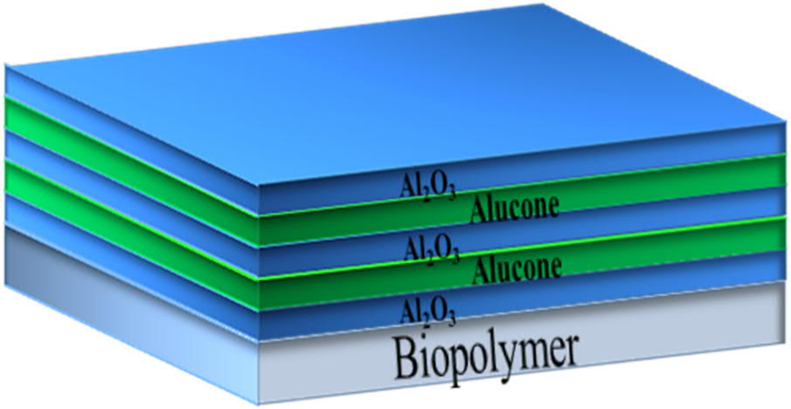
  ZnO-organic superlattice structures in a scale of 1~10 nm
  → **Suppressed thermal conductivity/enhanced TE characteristics**

- **FLEXIBLE CRM-FREE MAGNETIC THIN FILMS**

  epsilon-Fe_2O_3-organic superlattice thin films → **enhanced mechanical properties without compromising the magnetic properies**

BIOBASED PACKAGING MATERIALS: Polylactic acid (PLA)

- biodegradable & sustainable
- **PROBLEM:** oxygen transmission rate too large:
  OTR = 400 cm^3/m^2 $d10^5$ Pa
- **SOLUTION:**
  thin (25 nm) **ALD-Al_2O_3** coating:
  OTR = 20 cm^3/m^2 $d10^5$ Pa
- **PROBLEM:** strain induces cracks & deteriorates barrier properties of ALD-Al_2O_3



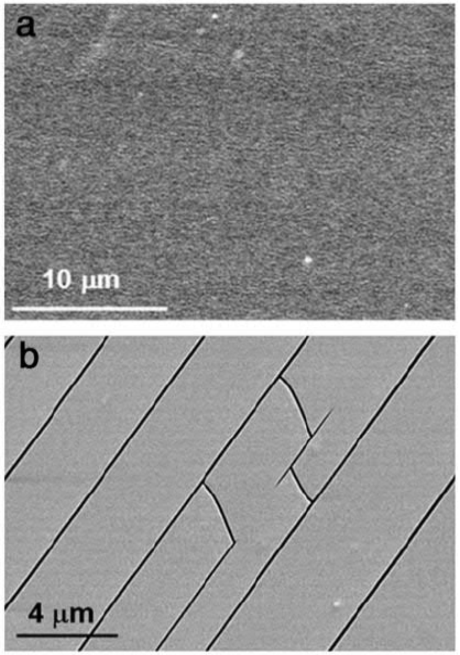
- **SOLUTION:**
  Al_2O_3 + alucone
  ($-Al-O-CH_3-CH_3-O-$)
  nanolaminate coating
  by ALD/MLD

3 % strain

25 nm Al_2O_3

20

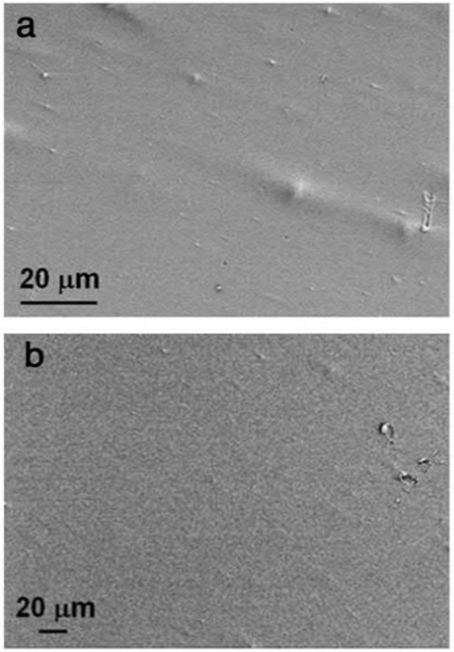
300



25 nm Al_2O_3-alucone

20

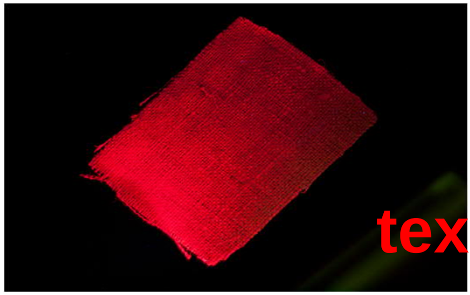
30

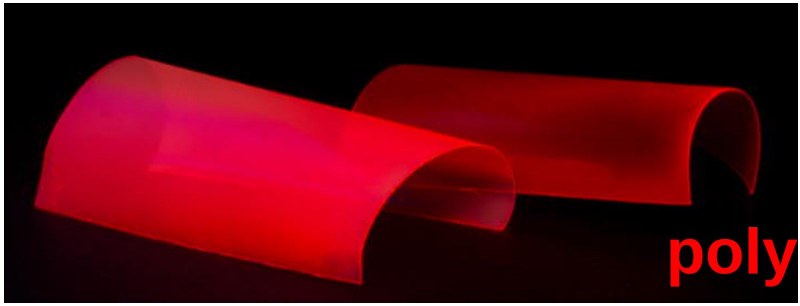


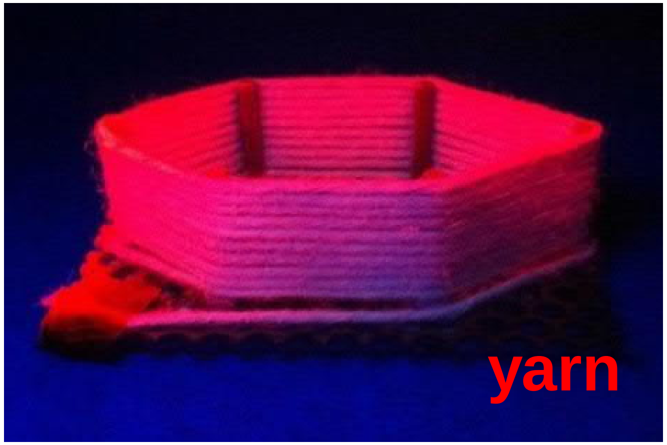
M. Vähä-Nissi, P. Sundberg,
T. Hirvikorpi, J. Sievänen,
A. Sood, M. Karppinen & A. Harlin,
Thin Solid Films **520**, 6780 (2012).

PHOTOLUMINESCENCE: Flexible Eu-hybrid thin films

PRECURSORS:
Eu(thd)$_3$ + pyridinedicaboxylic acid

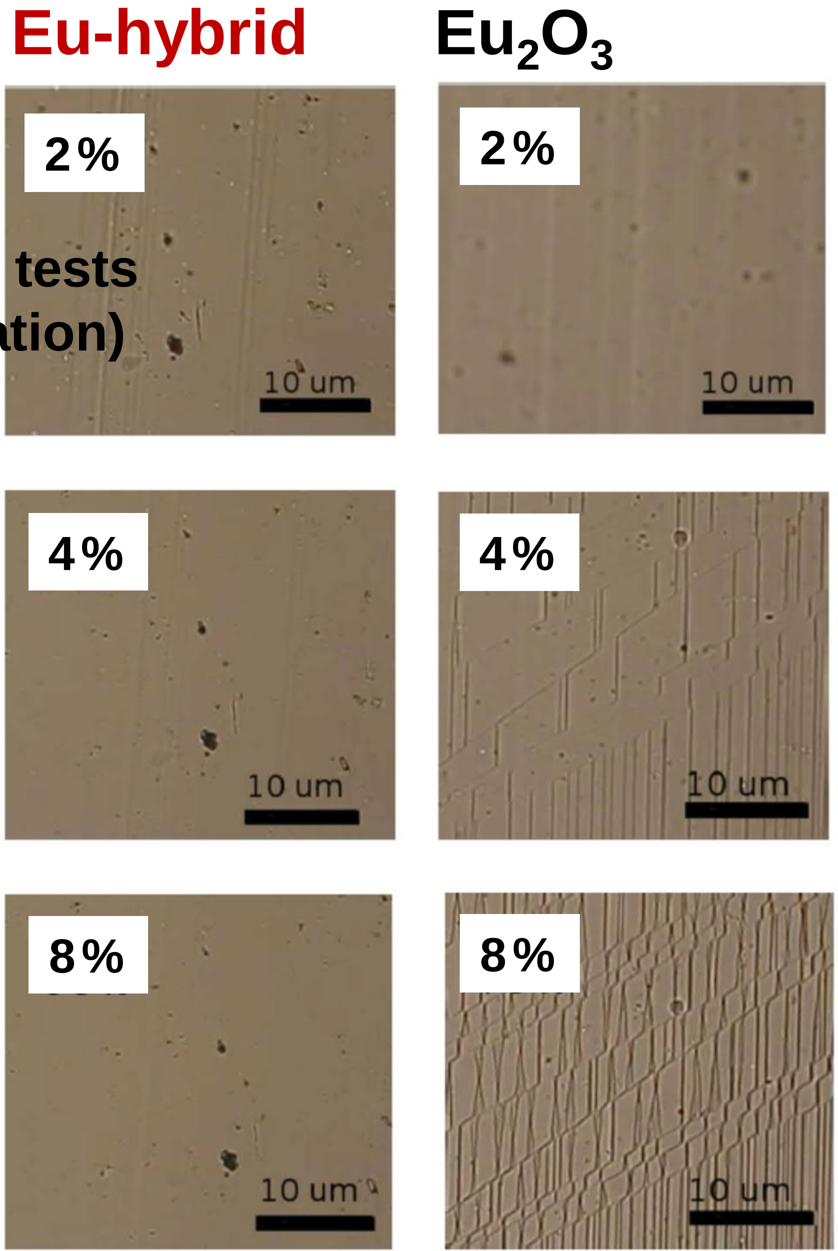




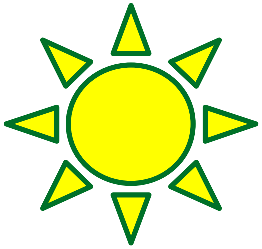


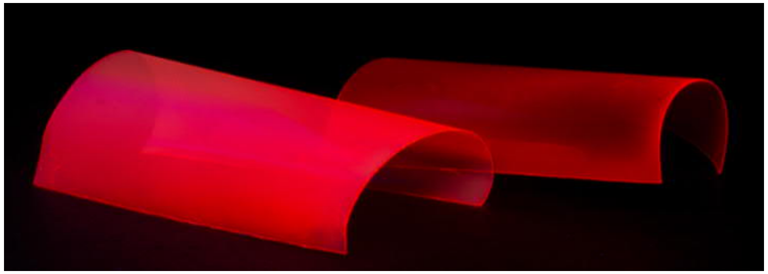
Z. Giedraityte, P. Sundberg & M. Karppinen,
J. Mater. Chem. C **3**, 12316 (2015).

Tensile tests (elongation)

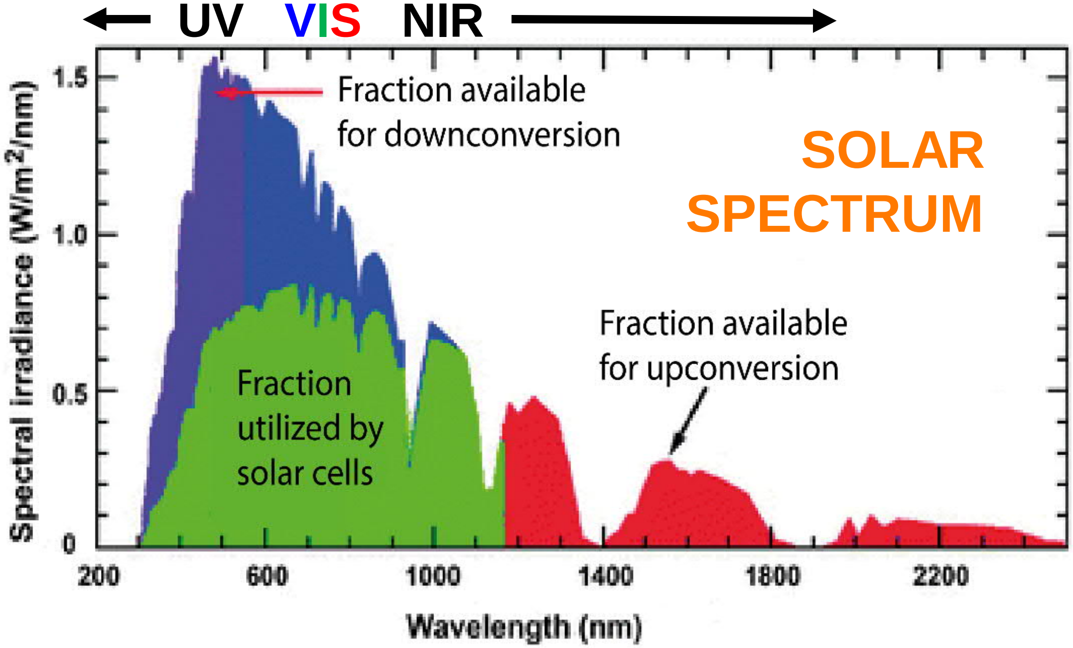


PHOTOLUMINESCENCE:
VIS from UV radiation

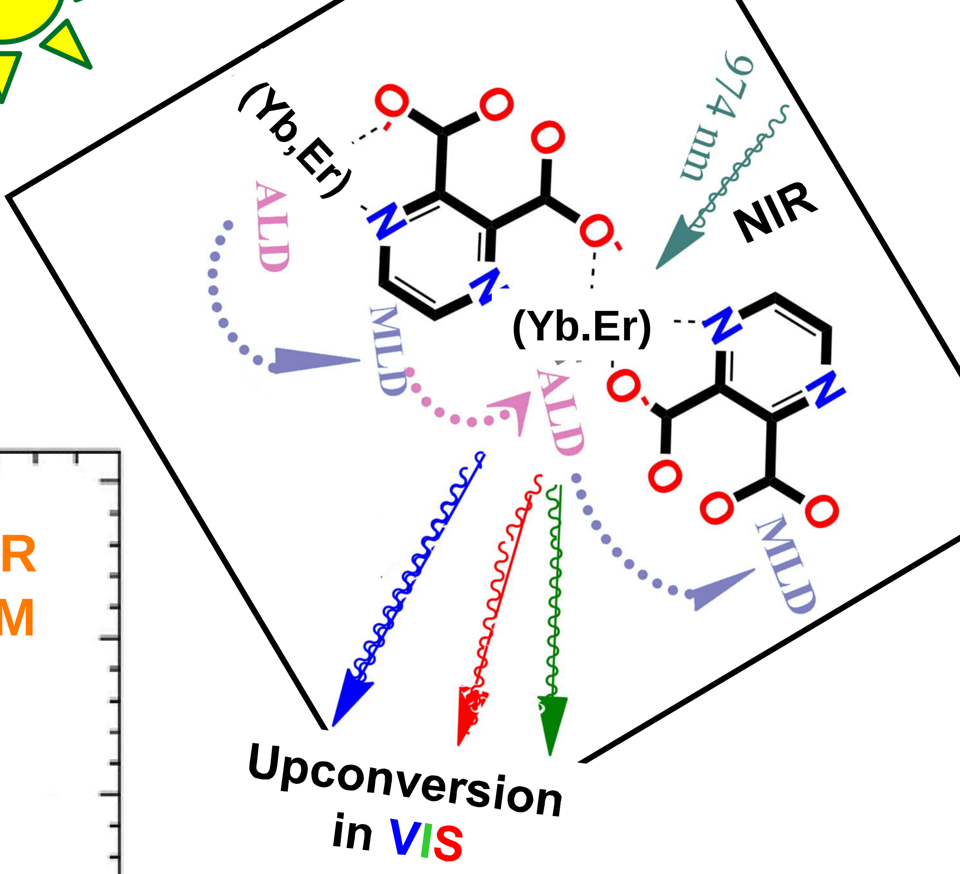




Eu-organic ALD/MLD films



UPCONVERSION:
VIS from NIR radiation



(Yb,Er)-organic ALD/MLD films

Aalto University
School of Engineering

A. Ghazy, M. Safdar, M. Lastusaari, A. Aho, A. Tukiainen, H. Savin, M. Guina & M. Karppinen, Luminescent $(Er,Ho)_2O_3$ thin films by ALD to enhance the performance of silicon solar cells, *Solar Energy Materials & Solar Cells* **219**, 110787 (2021).

- **Metal Coordination Complex**

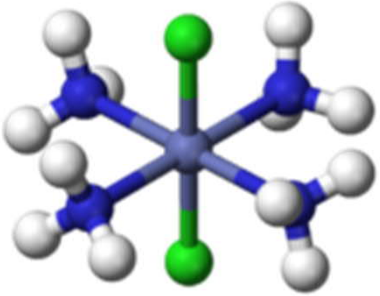
  - central metal atom + ligands

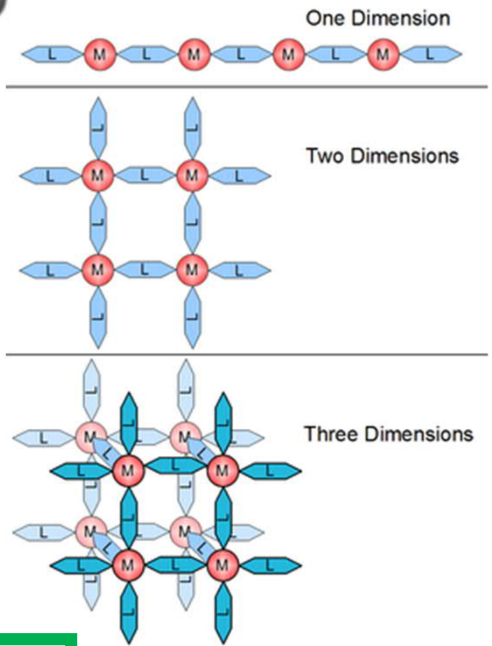
- **Coordination Network**

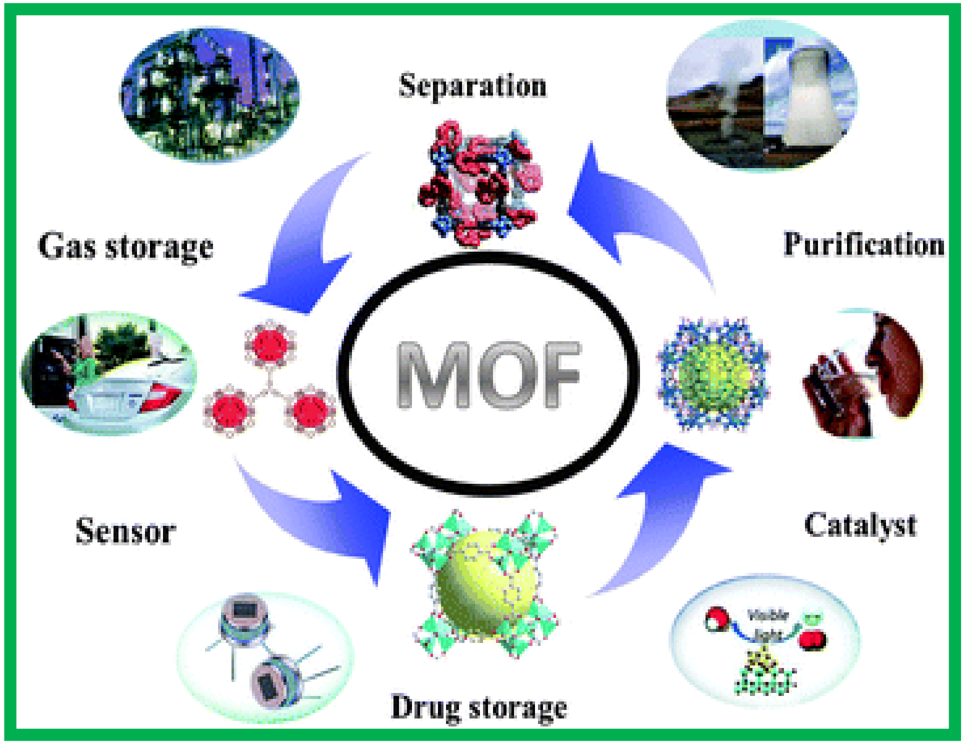
  - organic ligands act as linkers
  - 1D, 2D or 3D materials

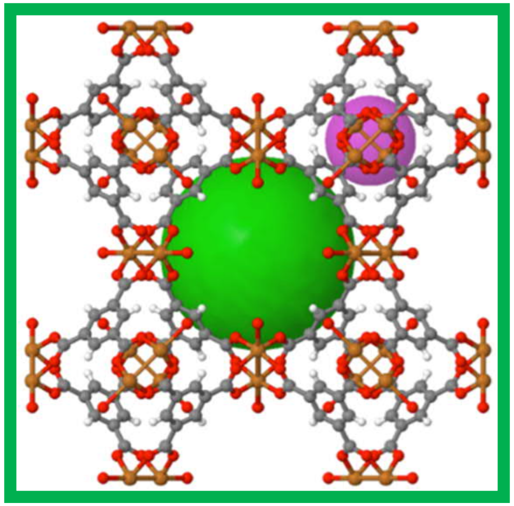
- **Metal Organic Framework (MOF)**

  - highly porous materials
  - attractive application possibilities

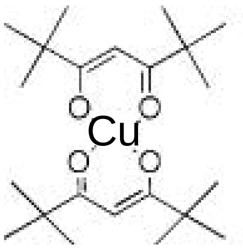




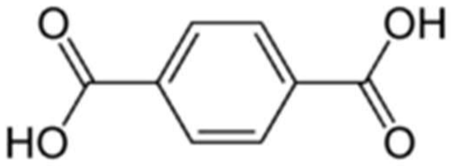




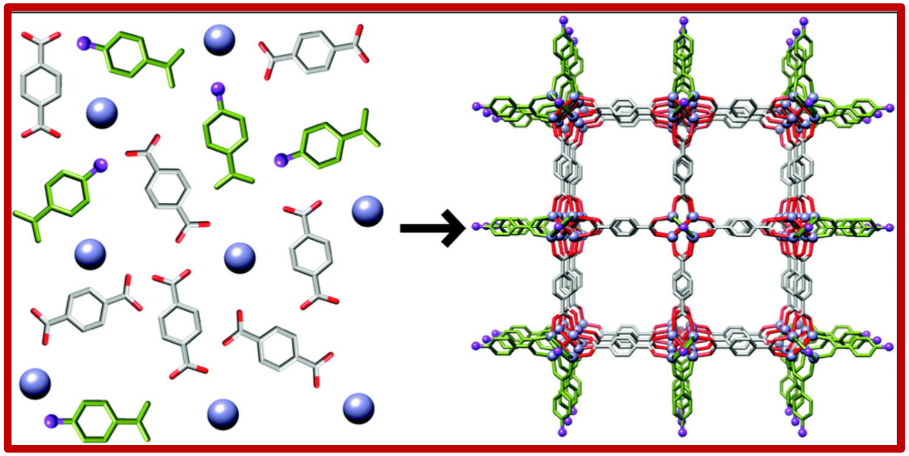
PRECURSORS for ALD/MLD



$Cu(thd)_2$



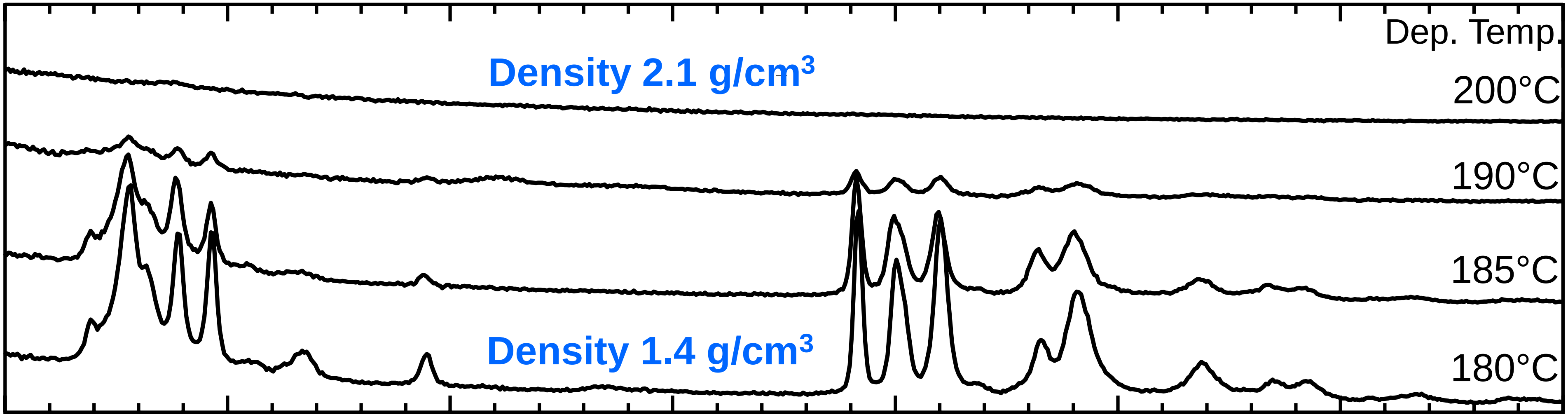
Terephthalic acid (TPA)

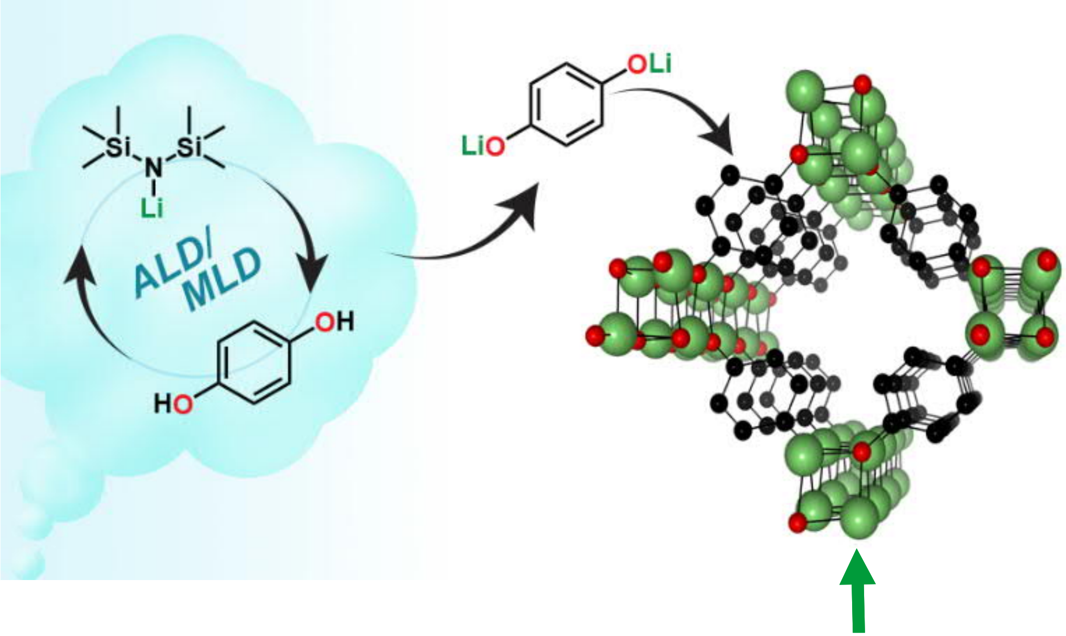


MOF

METAL-ORGANIC FRAMEWORK

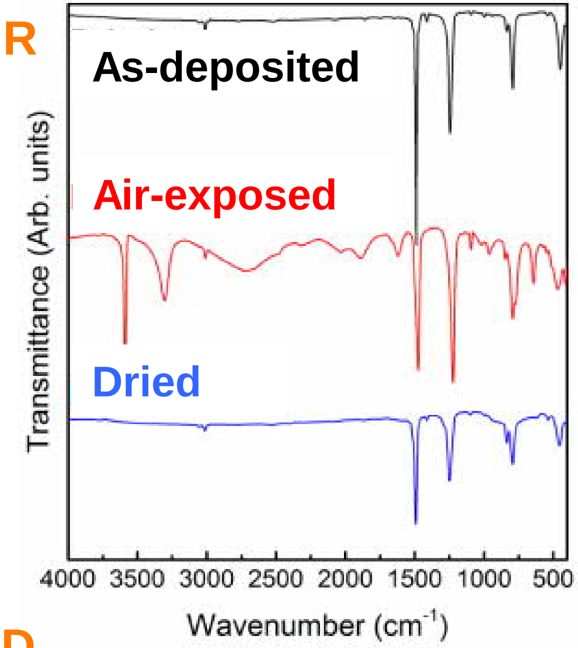
E. Ahvenniemi & M. Karppinen,
Chem. Commun. **52**, 1139 (2016).



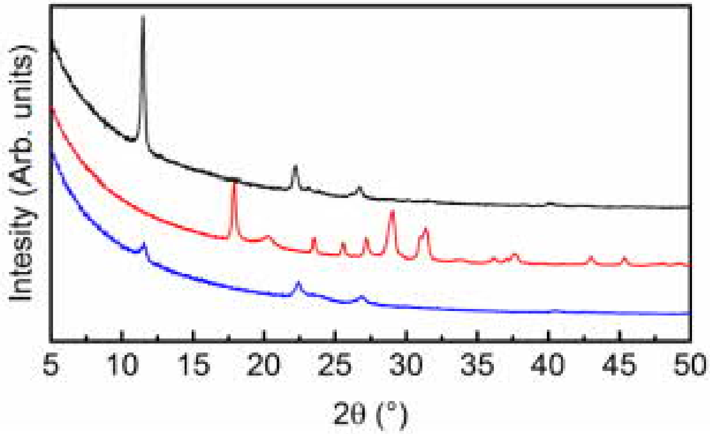


3-coord. Li-site

FTIR



XRD



Structure predicted by DFT

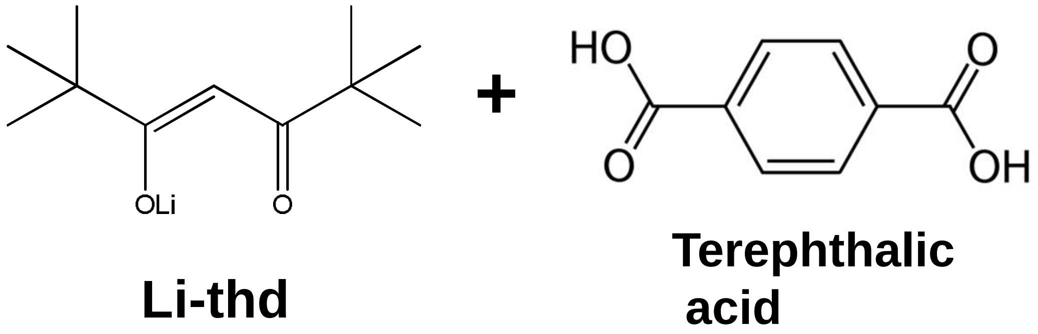
Li + Hydroquinone

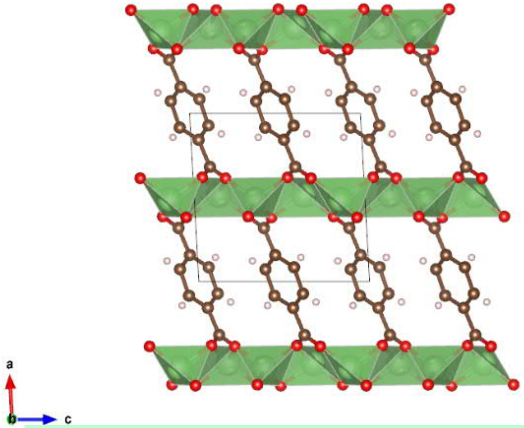
- **Crystalline films**
- **NOT synthesized by any other technique**
- **Under-coordinated Li-site**
- **Reversible water absorption (gas absorption)**
- **Potential application: Li-ion battery cathode**

M. Nisula, J. Linnera, A.J. Karttunen & M. Karppinen, Lithium aryloxide thin films with guest-induced structural transformation by ALD/MLD, *Chemistry – A European Journal* **23**, 2988 (2017).

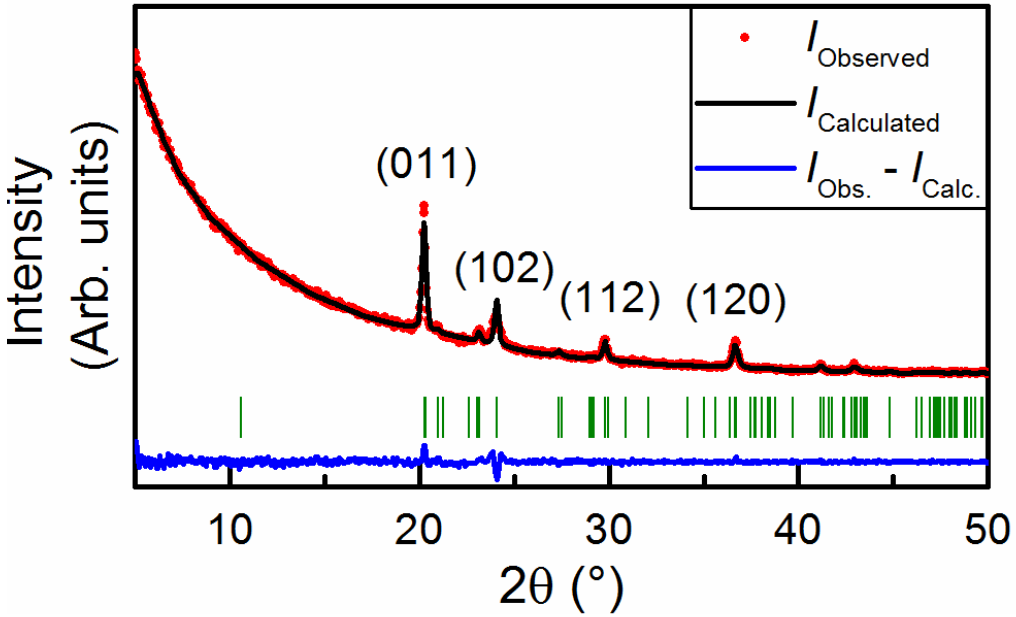
ANODE
Li-terephthalate

ALD/MLD:
Li-thd + TPA





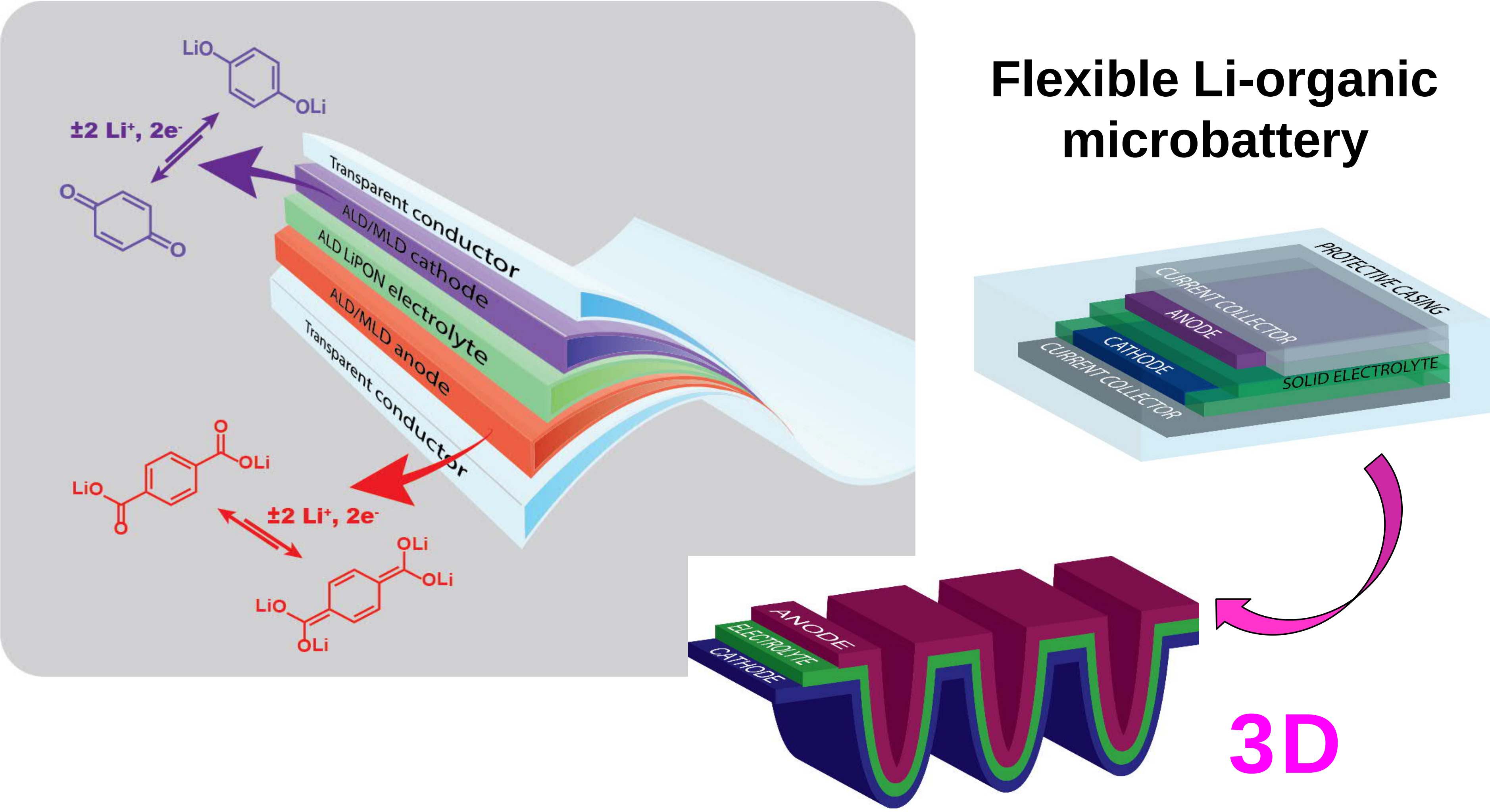
Layered structure with alternating layers of LiO_4 tetrahedra & benzene-rings



Aalto University
School of Chemical Technology

M. Nisula & M. Karppinen, Atomic/molecular layer deposition of lithium terephthalate thin films as high rate capability Li-ion battery anodes, *Nano Lett.* **16**, 1276 (2016).

Flexible Li-organic microbattery



3D

HIGH POWER & ENERGY DENSITY

Aalto University
School of Chemical
Technology

M. Nisula and M. Karppinen, In-situ lithiated quinone cathode for ALD/MLD-fabricated high-power thin-film battery, *J. Mater. Chem. A* **6**, 7027 (2018).

Inorganic-Organic INTERFACES:

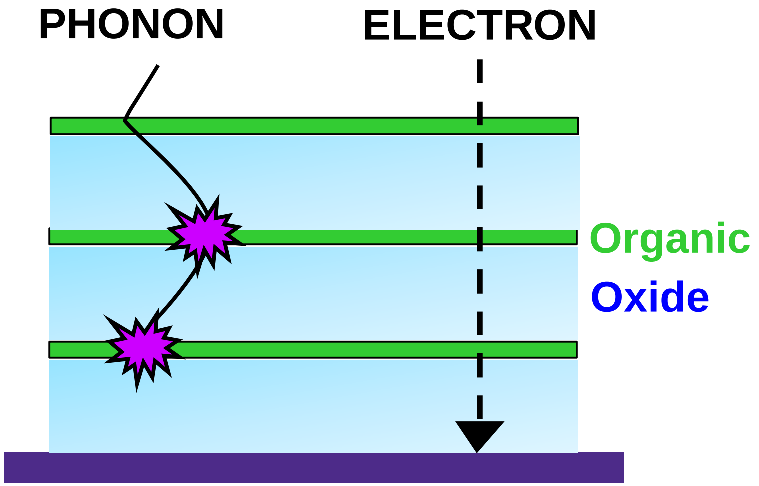
Reduction of Thermal Conductivity

- **Thermal conductivity (κ) is important: thermal barriers, thermoelectrics, etc.**
- **Interfaces in the form of superlattice: metal oxide layers & organic layers**
- **Proof-of-concept data: ZnO:benzene in a scale of 1 ~ 20 nm for ZnO**

Thermoelectric figure-of-merit

$$\boxed{ZT = \frac{S^2\sigma}{\kappa_e + \kappa_l} T}$$

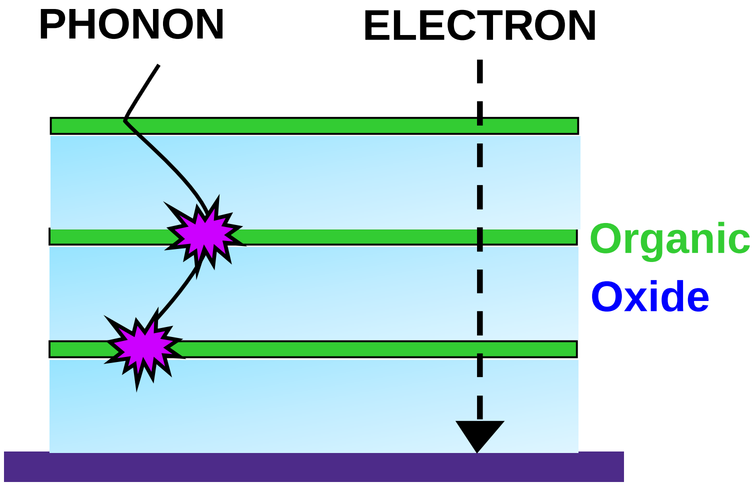
For oxides: κ_l large !

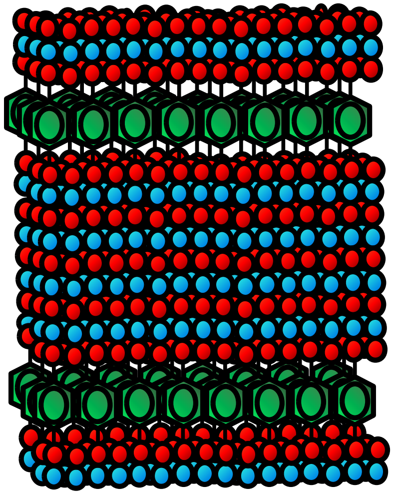


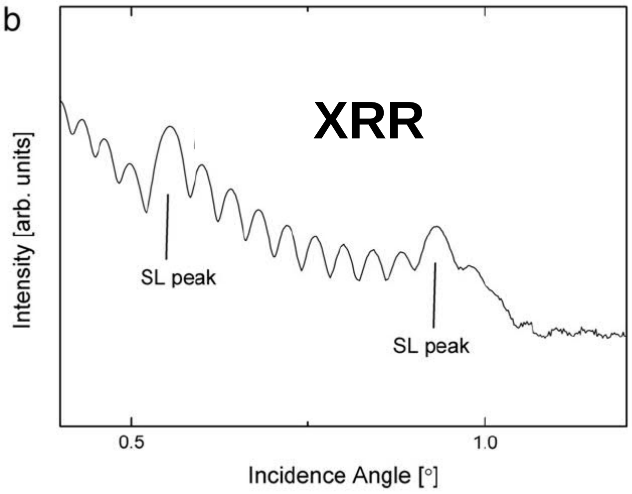
T. Tynell, A. Giri, J. Gaskins, P.E. Hopkins, P. Mele, K. Miyazaki & M. Karppinen, Efficiently suppressed thermal conductivity in ZnO thin films via periodic introduction of organic layers, ***J. Mater. Chem. A* 2**, 12150 (2014).

THERMOELECTRIC MATERIALS

- **High electrical conductivity & Low thermal conductivity**
  → Difficult combination to be achieved with conventional materials
- **ALD/MLD thin-film technology → nanoscale SUPERLATTICE (SL):**
  - thermoelectric oxide layers (ZnO) by ALD & organic (benzene) layers by MLD
  - thermal conductivity decreases but electrical conductivity remains the same
- **XRR: we can see SL peaks as an indication of the regular ordered SL structure**







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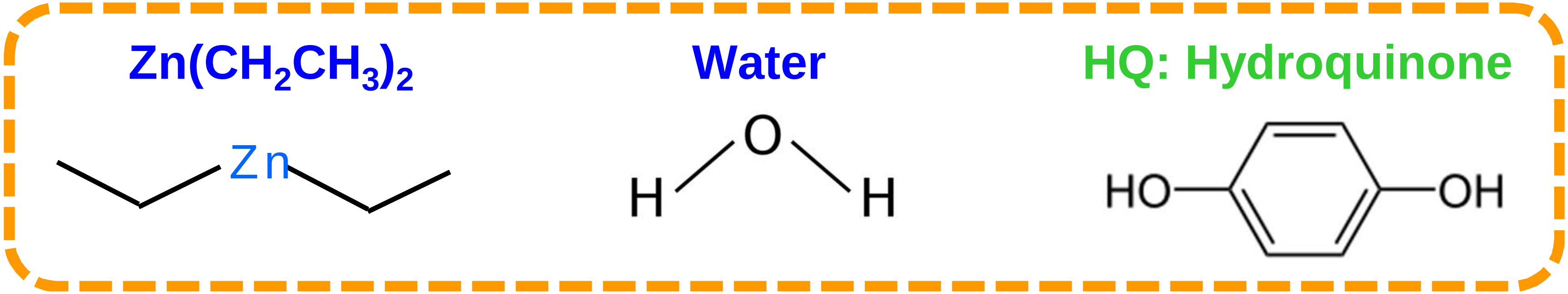
J.-P. Niemelä, A.J. Karttunen & M. Karppinen,
Inorganic-organic superlattice thin films for thermoelectrics,
J. Mater. Chem. C **3**, 10349 (2015).

ALD/MLD for ZnO : Benzene superlattice



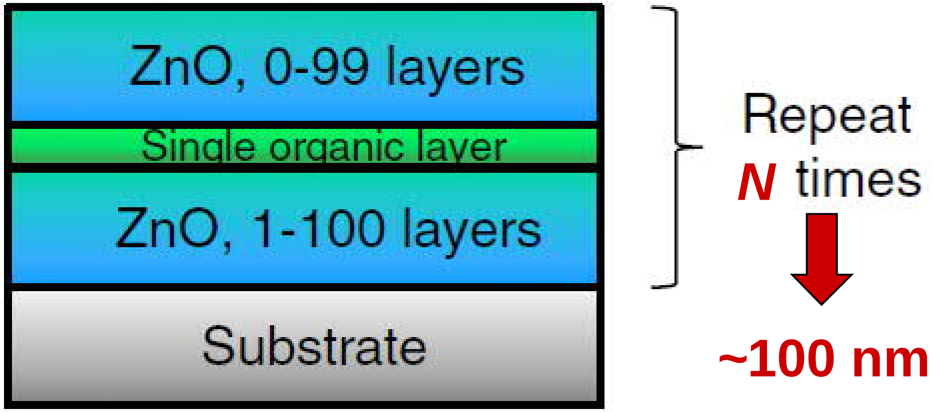
$Zn(CH_2CH_3)_2$

Water

HQ: Hydroquinone

DEPOSITIONS

- 220 °C
- 600 ALD/MLD cycles in total



ZnO, 0-99 layers

Single organic layer

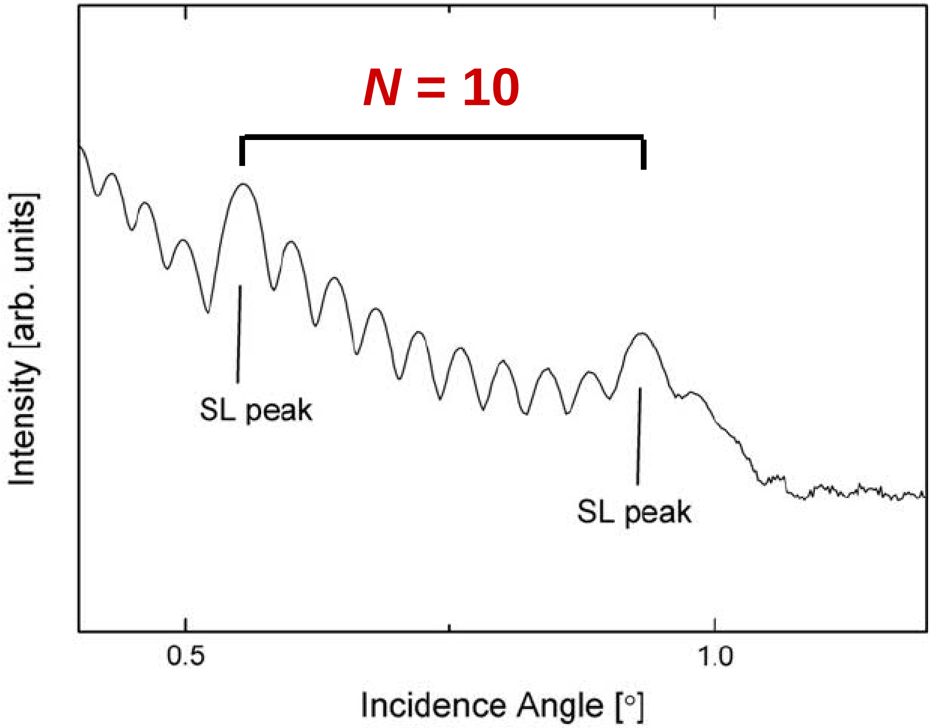
ZnO, 1-100 layers

Substrate

Repeat *N* times

~100 nm

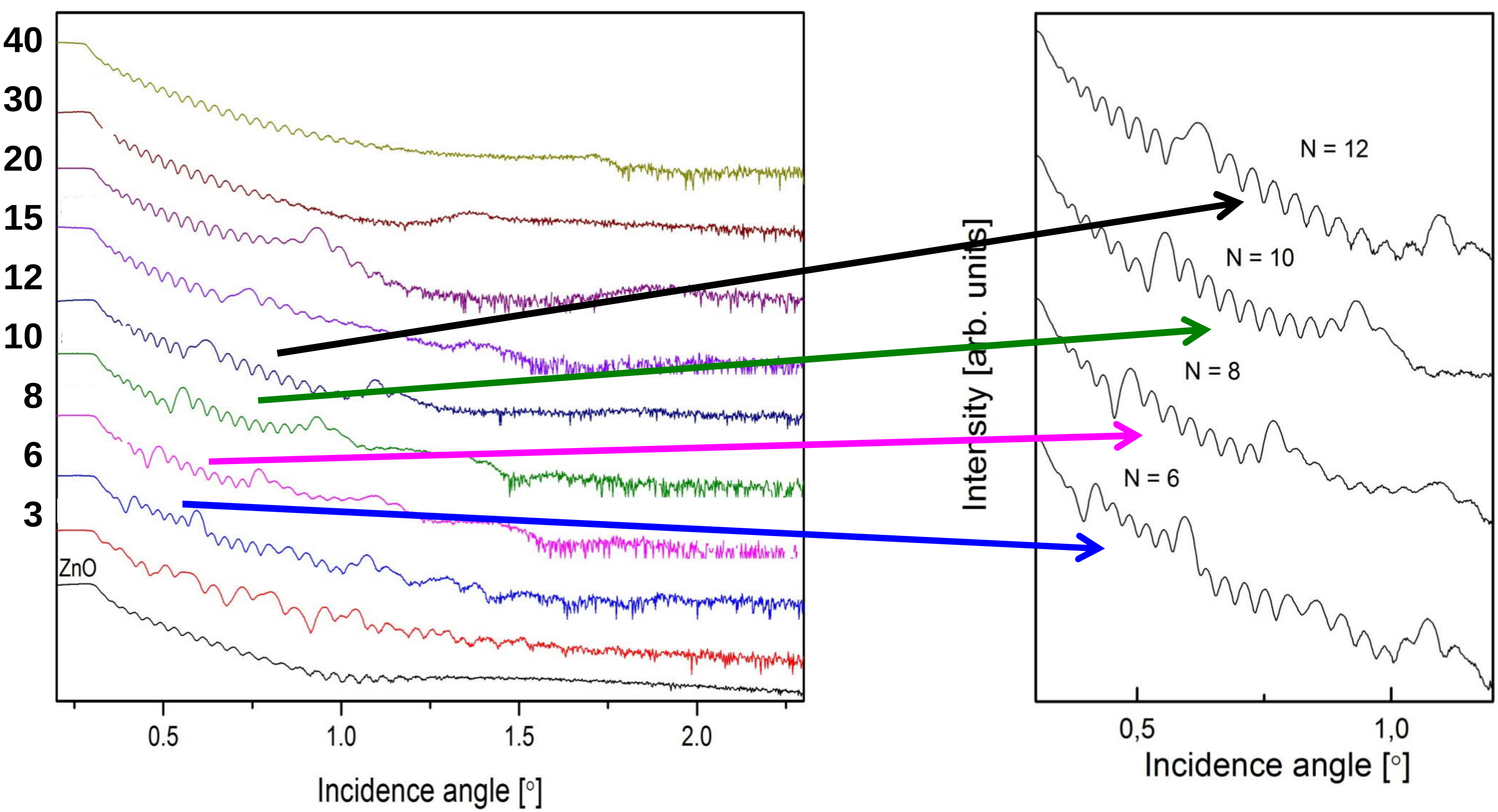
XRR: X-ray Reflectivity



XRR:

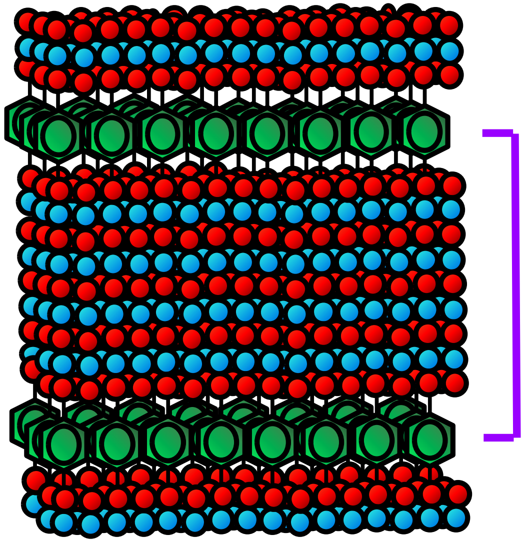
- **We can see/count the number (N) of ”superlayer” units in the SL thin film; most clearly for N = 6 to 12; for N > 12 the oscillations start to overlap**
- **NOTE: for ZnO no SL peaks are seen**

N x [ZnO : benzene]



T. Tynell, I. Terasaki, H. Yamauchi & M. Karppinen, *J. Mater. Chem. A* **1**, 13619 (2013).

ZnO : benzene



SUPERLATTICE PERIOD

99 : 1 → 16 nm
49 : 1 → 8 nm
29 : 1 → 5 nm
9 : 1 → 2 nm
4 : 1 → 1 nm

THERMAL CONDUCTIVITY (at RT)

Sample	**K [W m^{-1} K^{-1}]**
ZnO	~43
ZnO : benzene **(99 : 1)**	7.1
ZnO : benzene **(49 : 1)**	4.1
ZnO : benzene **(29 : 1)**	3.1
ZnO : benzene **(9 : 1)**	1.3
ZnO : benzene **(4 : 1)**	0.7

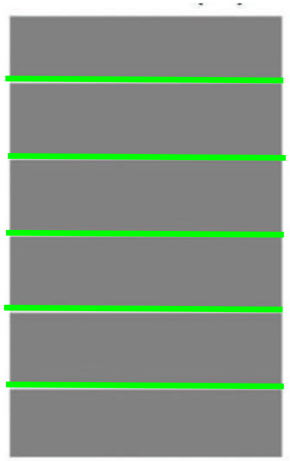
- T. Tynell, A. Giri, J. Gaskins, P.E. Hopkins, P. Mele, K. Miyazaki & M. Karppinen, ***J. Mater. Chem. A* 2**, 12150 (2014).
- A. Giri, J.-P. Niemelä, C.J. Szwejkowski, M. Karppinen & P.E. Hopkins, ***Phys. Rev. B* 93**, 024201 (2016).
- A. Giri, J.-P. Niemelä, T. Tynell, J. Gaskins, B.F. Donovan, M. Karppinen & P.E. Hopkins, ***Phys. Rev. B* 93**, 115310 (2016).

Using the ALD/MLD technique it is possible to perfectly control where within the ZnO film the organic (benzene) layers are placed → We can grow both regular superlattice films and irregular “gradient” ZnO-organic films. For example, in both of the following two films

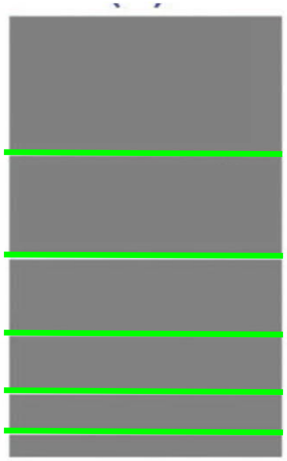
Total film thickness: ~105 nm
Number of organic layers: 5
Average ZnO layer thickness: ~17 nm

Superlattice: all ZnO layers ~17 nm (thermal conductivity
Gradient film: ZnO layers 9 ~ 28 nm

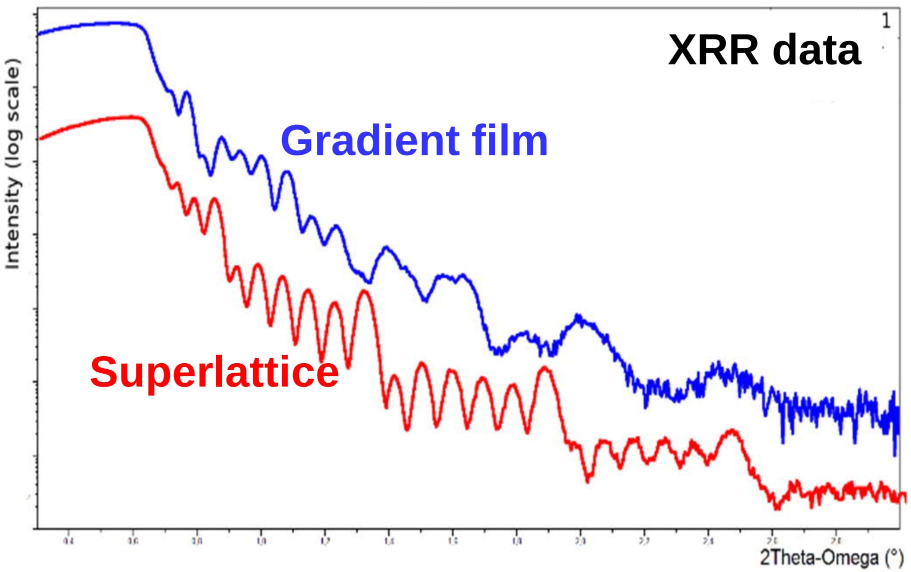
ONLY for the former the SL peaks are seen in XRR data



Superlattice



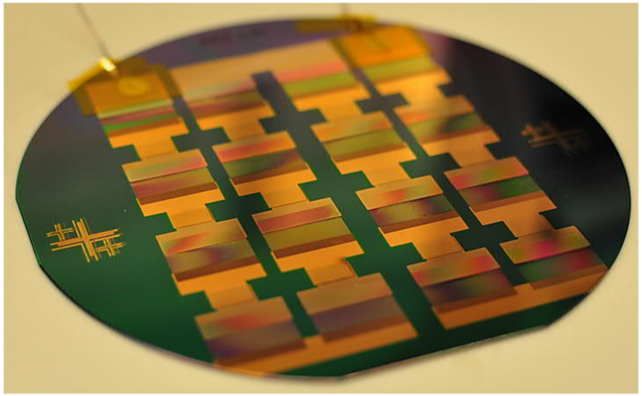
Gradient film



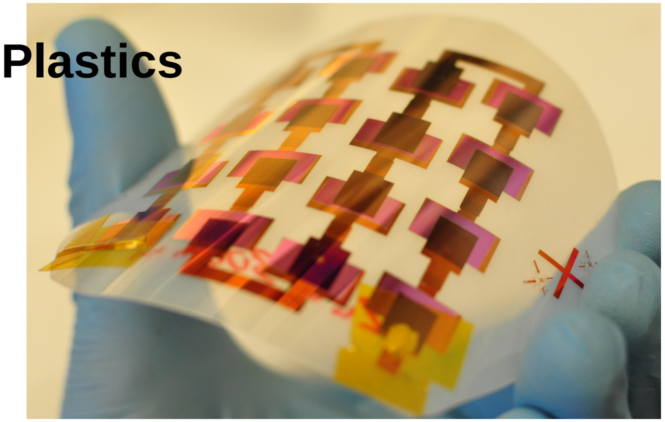
F. Krahl, A. Giri, J.A. Tomko, T. Tynell, P.E. Hopkins & M. Karppinen, Thermal conductivity reduction at inorganic-organic interfaces: from regular superlattices to irregular gradient layer sequences, *Adv. Mater. Interfaces* **5**, 1701692 (2018).

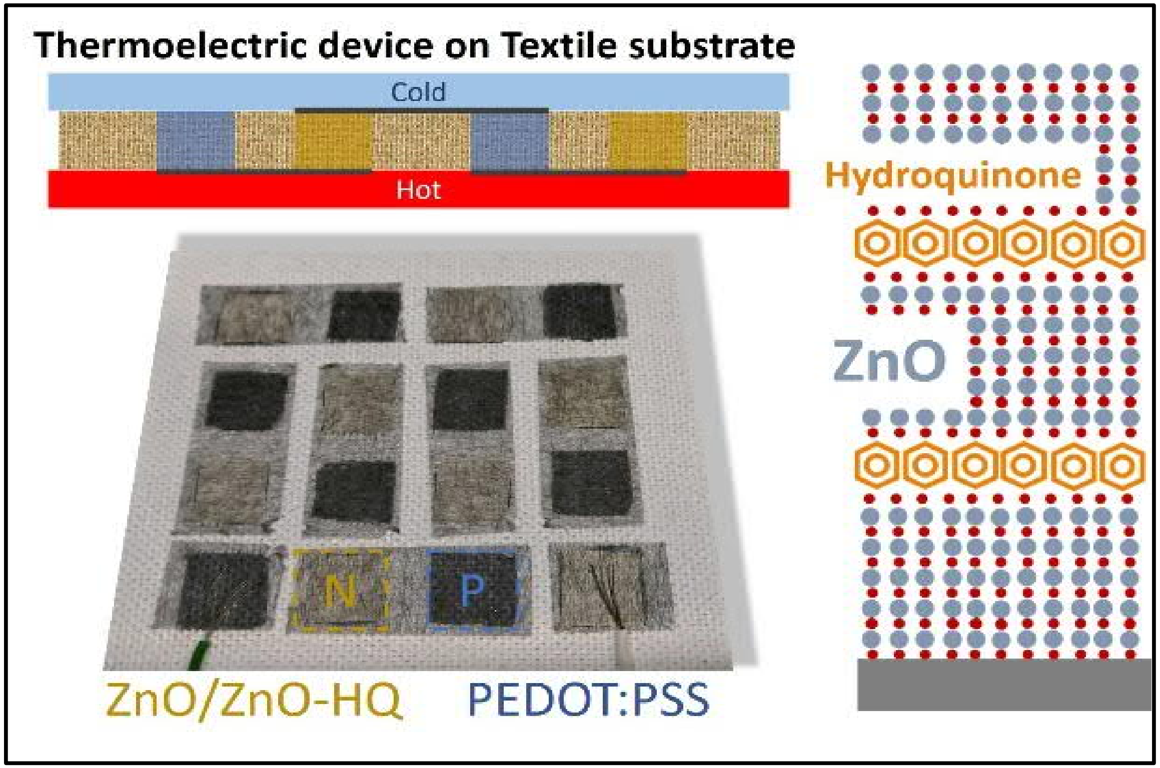
THERMOELECTRIC
MODULE

Silicon



Plastics





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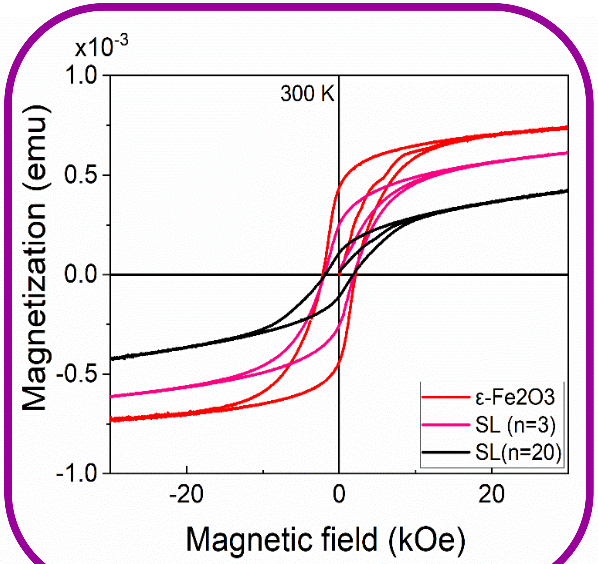
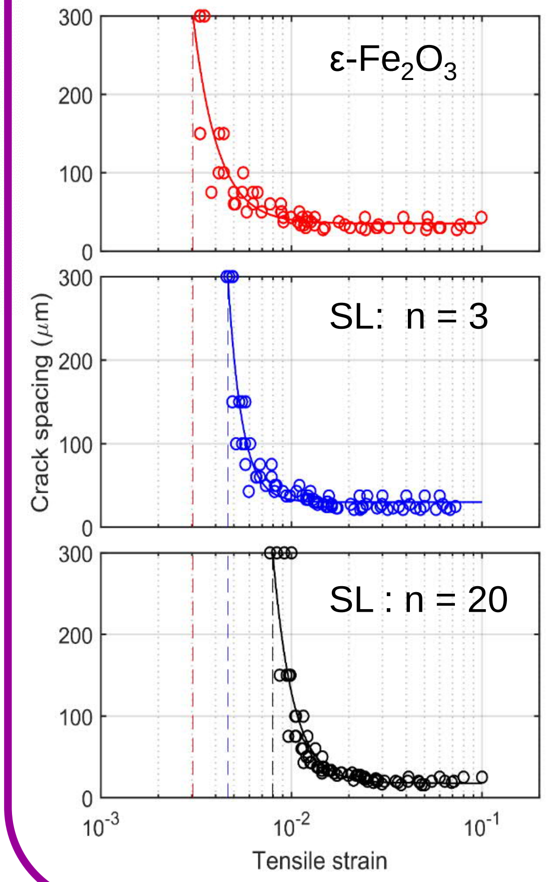
G. Marin, R. Funahashi & M. Karppinen,
Textile-integrated ZnO-based thermoelectric device using atomic layer deposition, *Advanced Engineering Materials* **22**, 2000535 (2020).

FLEXIBLE RT MAGNETIC films ε-Fe_2O_3:organic



HARD MAGNET: ε-Fe_2O_3:organic SL

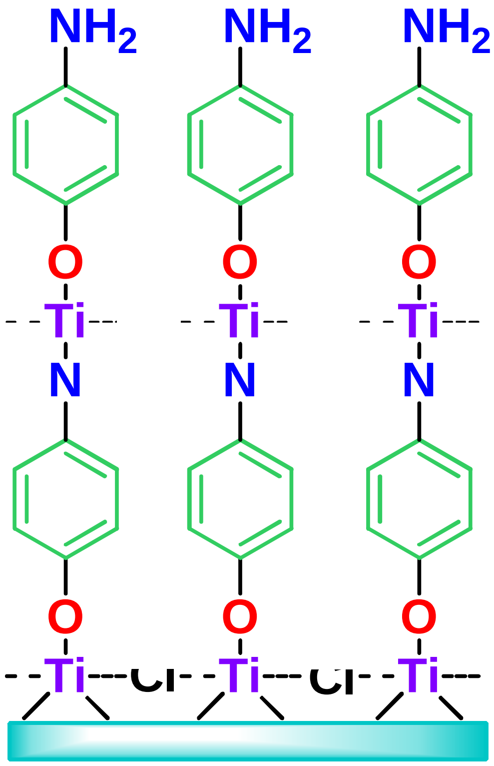


A. Philip, J.-P. Niemelä, G.C. Tewari, B. Putz, T.E.J. Edwards, M. Itoh, I. Utke & M. Karppinen, Flexible ε-Fe_2O_3-terephthalate thin-film magnets through ALD/MLD, *ACS Applied Materials & Interfaces* **12**, 21912 (2020).

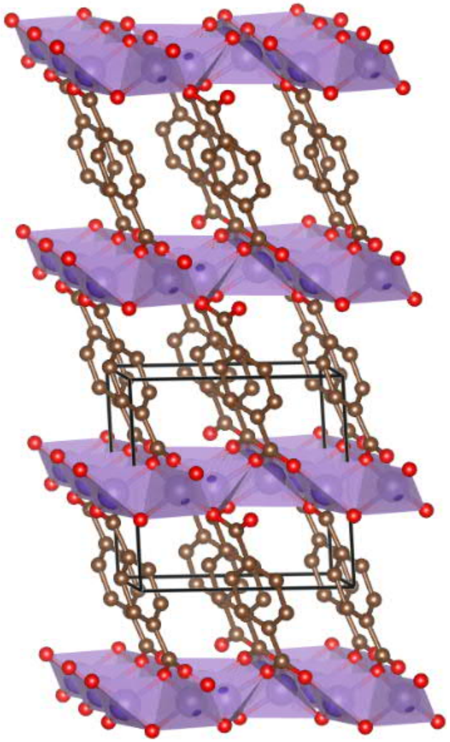
About the CHEMICAL BONDING in the films

- Covalent bonds
- Ionic bonds
- Hydrogen bonds

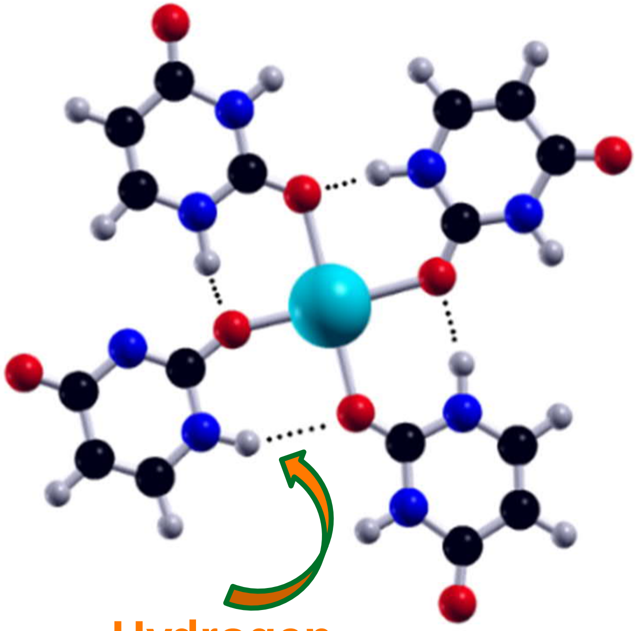
Ti + AP



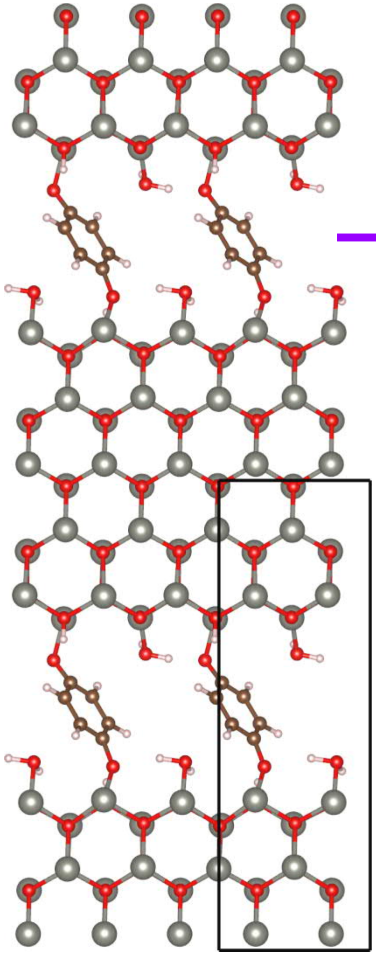
Li + TPA

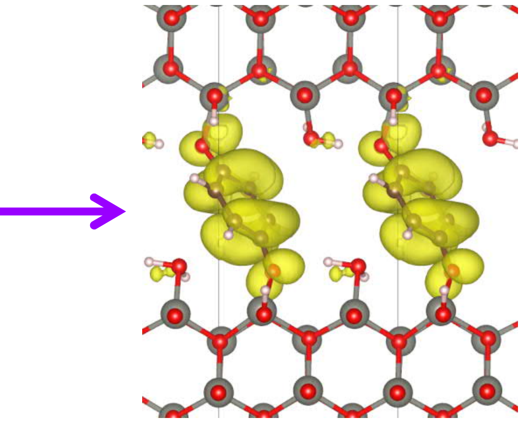


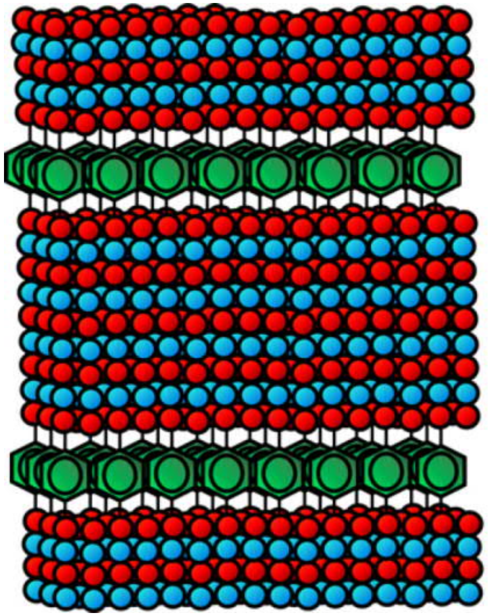
Na + Uracil



Hydrogen bonding







MODELLING

- **Computational** first-principles calculations
- **Atomic-level bonding models**
- **Band structures**
- **Prediction of physical properties**

A.J. Karttunen, T. Tynell & M. Karppinen, *J. Phys. Chem. C* 119, 13105 (2015).