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Flexible superlattice thin-film thermoelectrics by ALD/MLD (atomic/molecular layer deposition)

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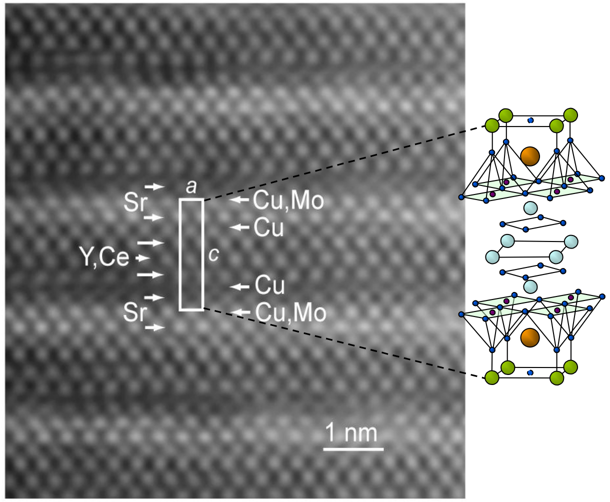
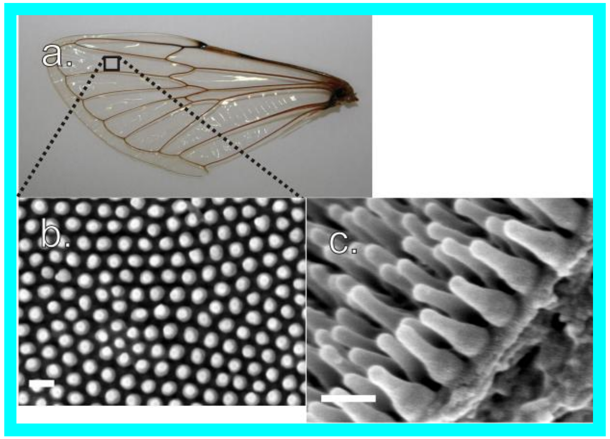
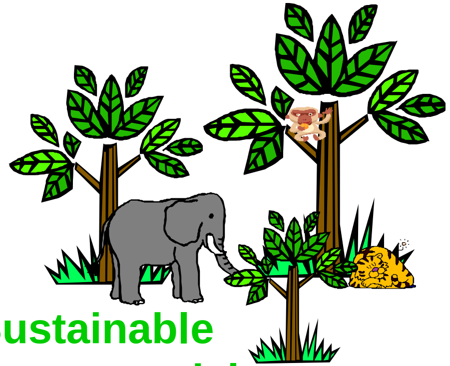
EPSRC Thermoelectric Network Meeting
Manchester, UK
February 14th, 2017





INORGANC CHEMISTRY

Aalto University



Sustainable energy materials

§ Novel Functional (bulk) Oxide Materials

- **high-T_c superconductors**
- **luminescence materials**
- **exotic magnetic materials (halfmetals, ferroelectrics)**
- **thermoelectric materials**
- **ionic conductors (Li-IB, SOFC, oxygen storage)**

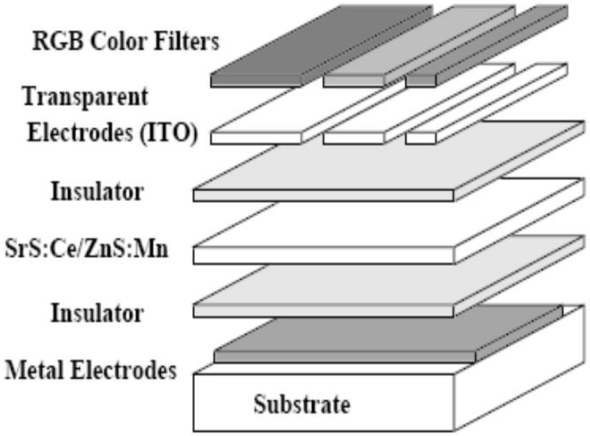
§ ALD (Atomic Layer Deposition) Thin Films

- **complex (ternary & quaternary) oxides**
- **oxide coatings on novel/exciting surfaces (carbon nanotubes, steel, polymers, biomaterials, etc.)**
- **inorganic/organic hybrid materials**

KEY CONCEPTS:
Layer-engineering & Oxygen-engineering & Nanostructuring

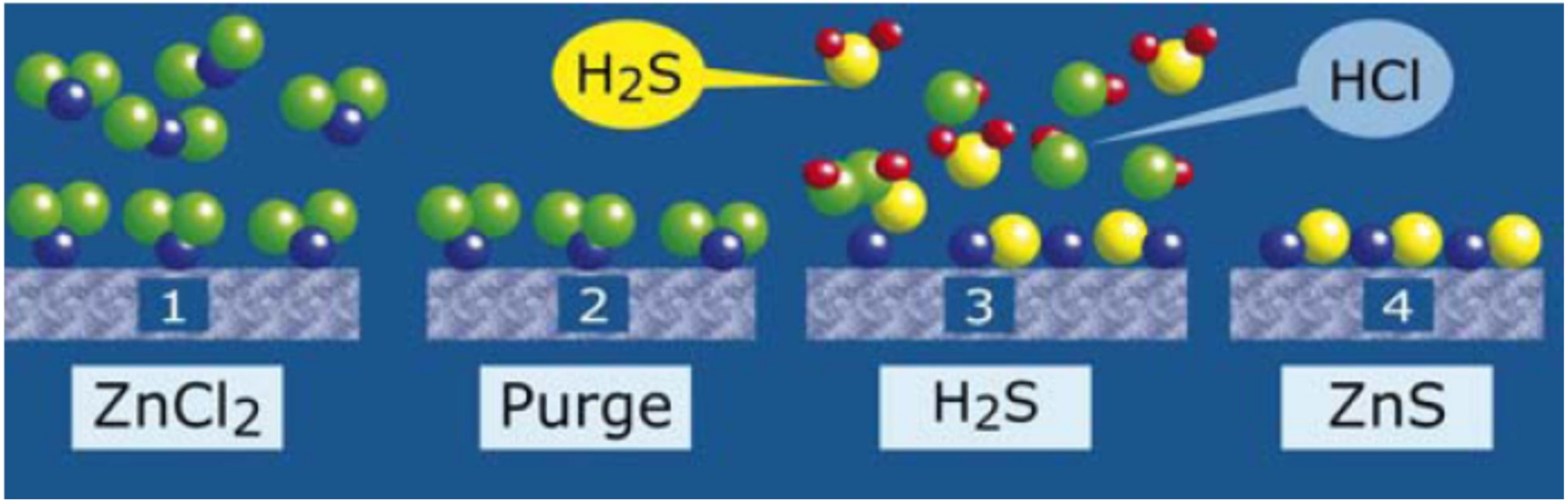
Atomic Layer Deposition (ALD) Thin-Film Technique

- **Gaseous precursors**
- **Self-limiting surface reactions**
- **Large-area homogeneous thin films with atomic-layer accuracy**



Electroluminescent display

Instrumentarium / Finlux / Planar



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

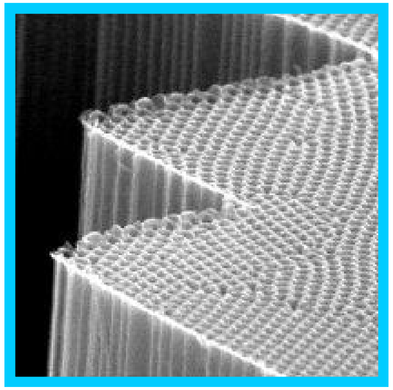
ADVANTAGES of ALD

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

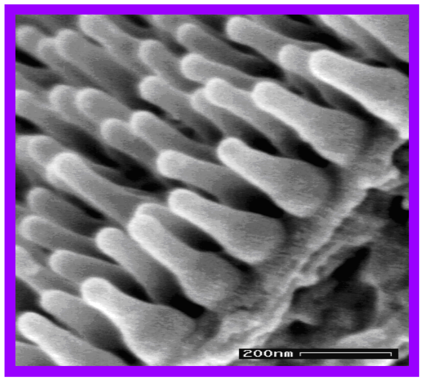
ELECTRONICS

NANO

- Excellent conformity



BIO

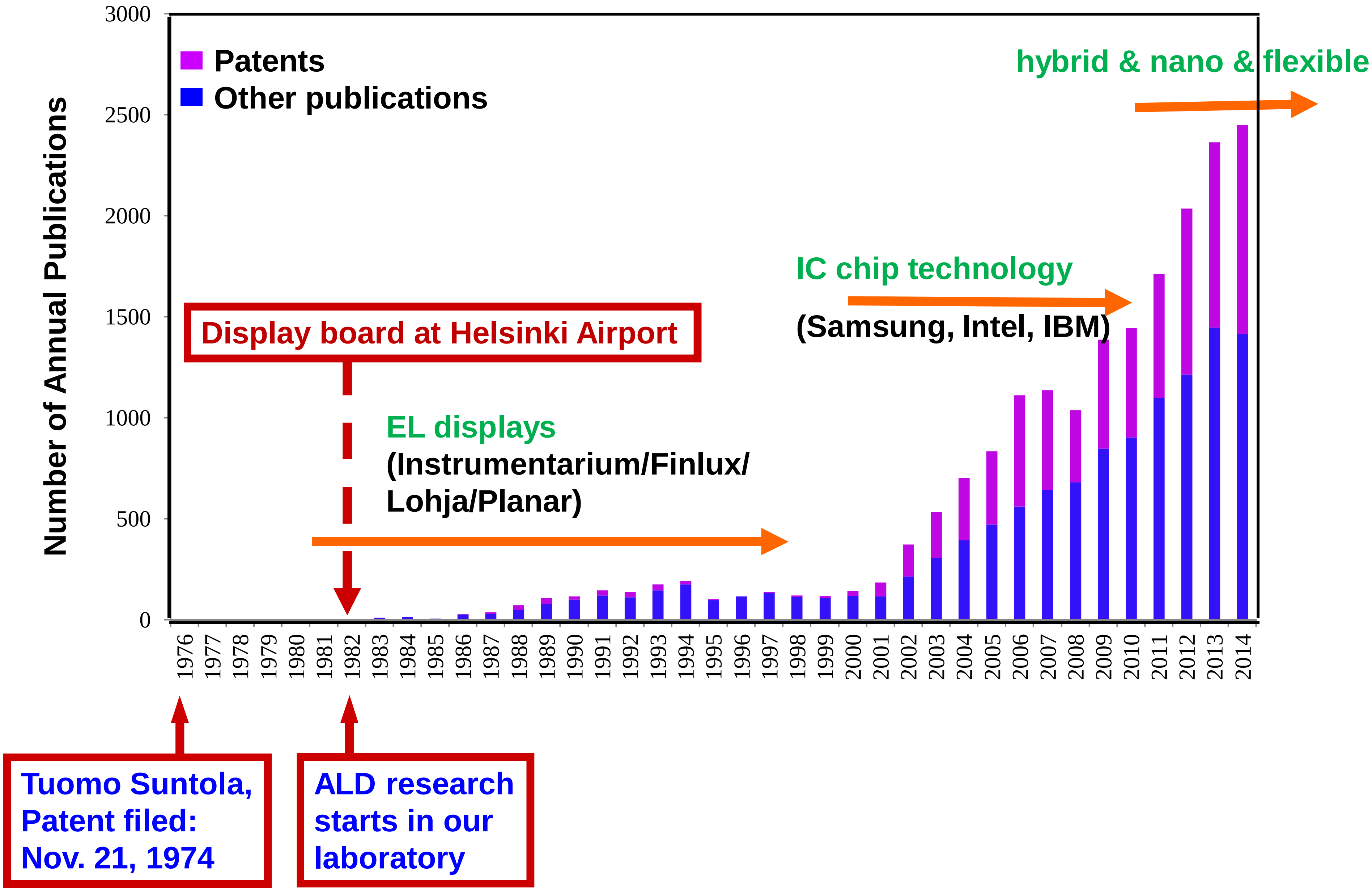


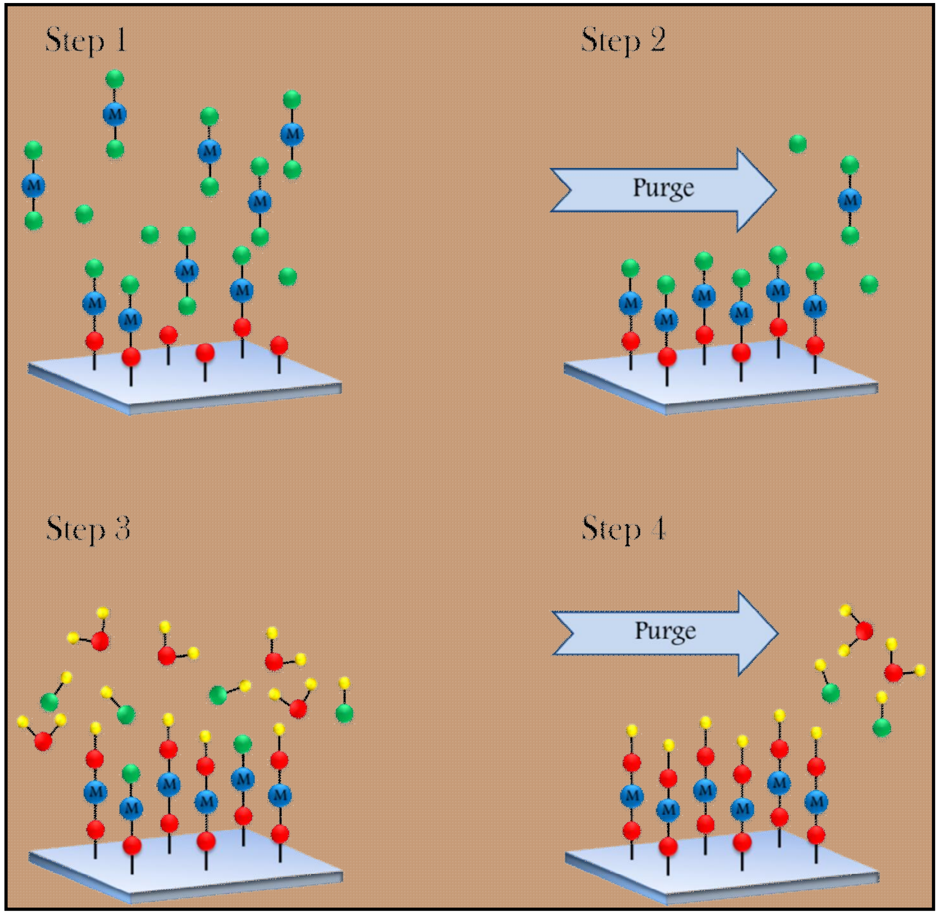
- Low deposition temperature
- Gentle deposition process

- Organic/polymer films
- Inorganic/organic hybrid materials

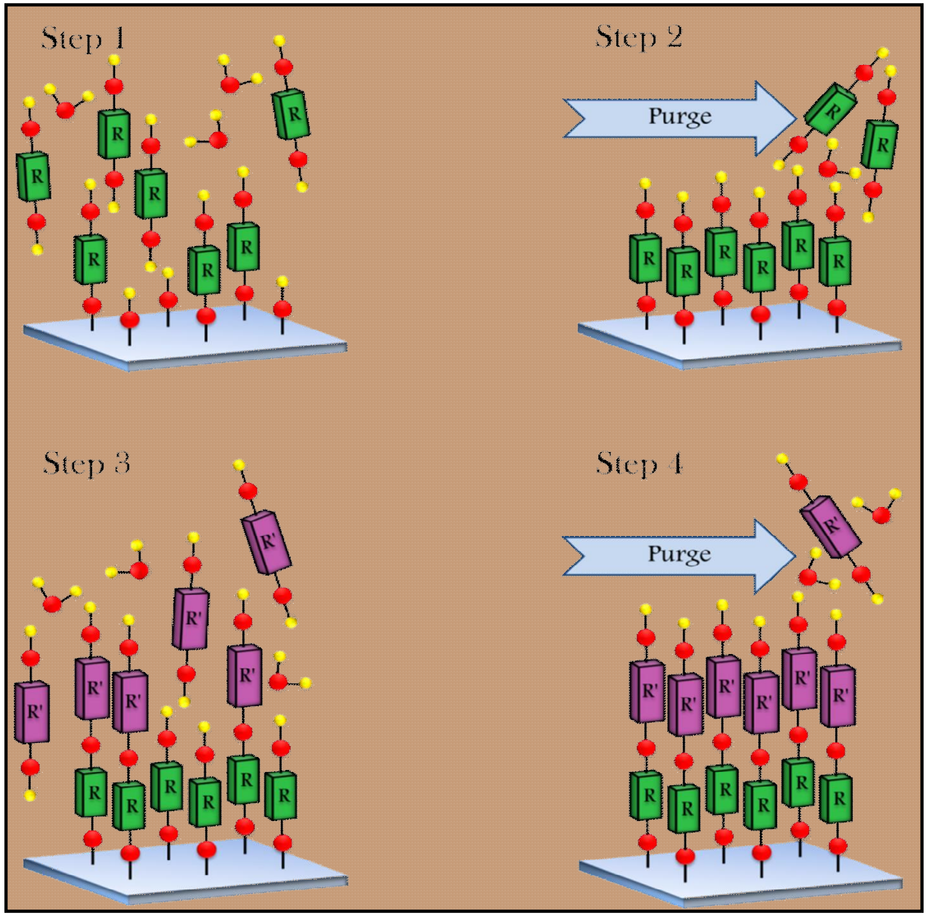
NEW

”History of ALD Technology”





ALD (Atomic Layer Deposition)

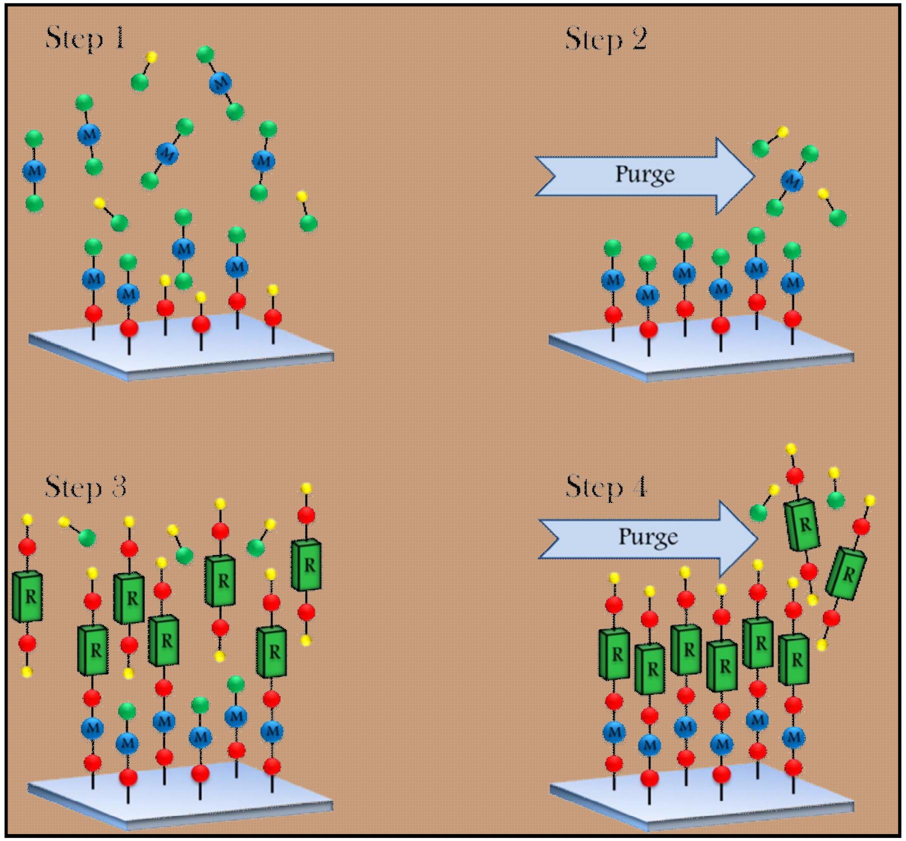


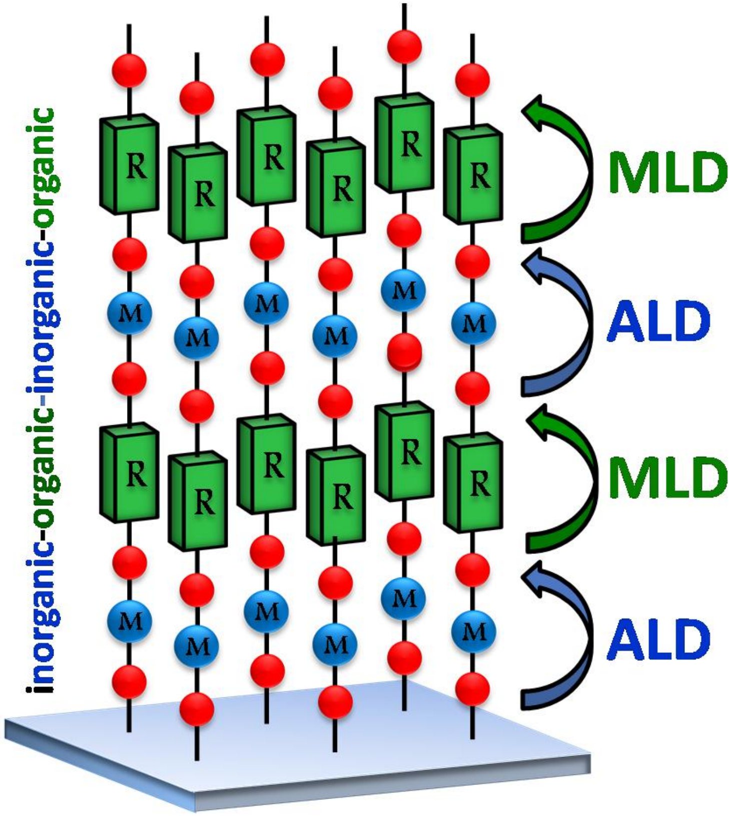
MLD (Molecular Layer Deposition)

High-quality INORGANIC thin films with atomic level control

ORGANICS !

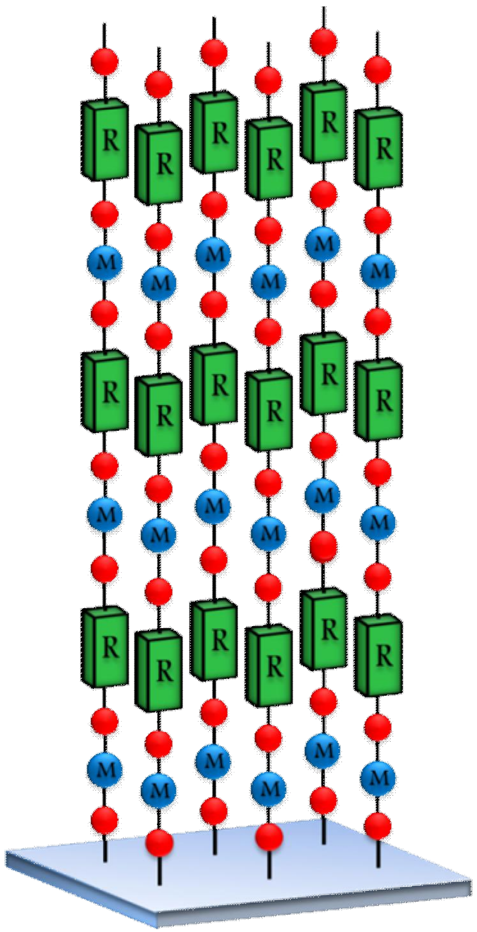
Inorganic-Organic Hybrid Thin Films by Combined ALD/MLD





FLEXIBLE MULTIFUNCTIONAL HYBRID MATERIALS !!!

ALD/MLD PRECURSORS



INORGANICS

$Al(CH_3)_3$ (TMA)

$Zn(CH_2CH_3)_2$ (DEZ)

$TiCl_4$

Ln (Eu, Er, …)

Fe, Mn, Co, Cu, …

Li, Na, K, Mg, Ca, …

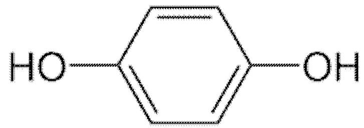
ORGANICS

Alcohols: –OH

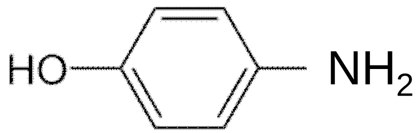
Carboxylic acids: –COOH

Diamines: $–NH_2$

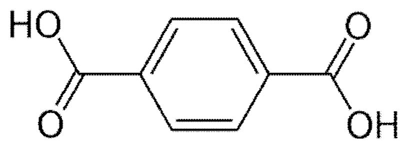
HQ: Hydroquinone



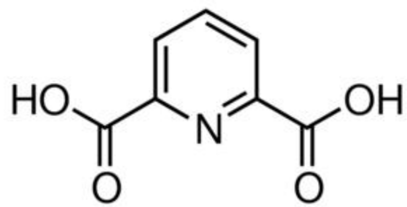
AP: Aminophenol



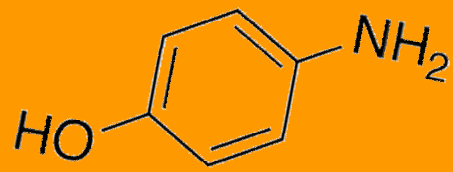
TPA: Terephthalic acid

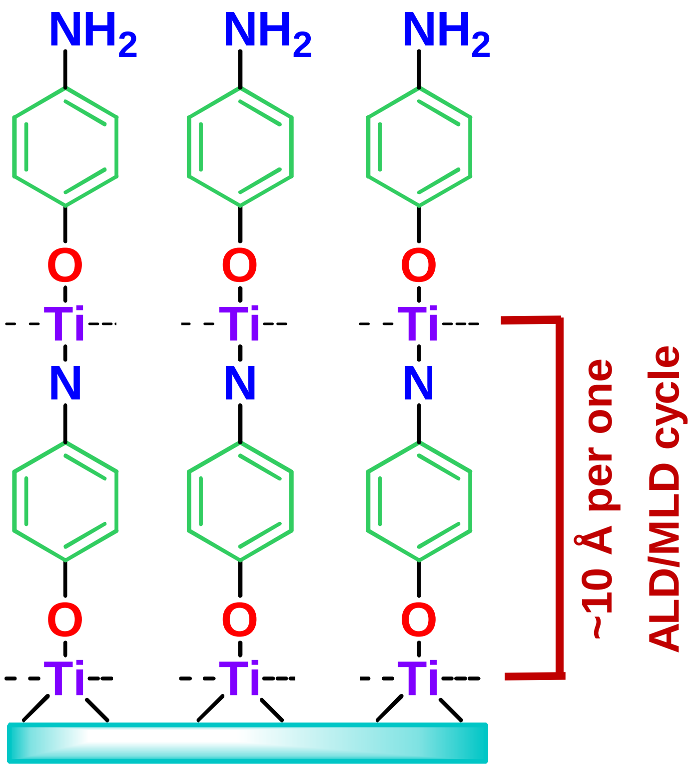


Pyridinedicarboxylic acid

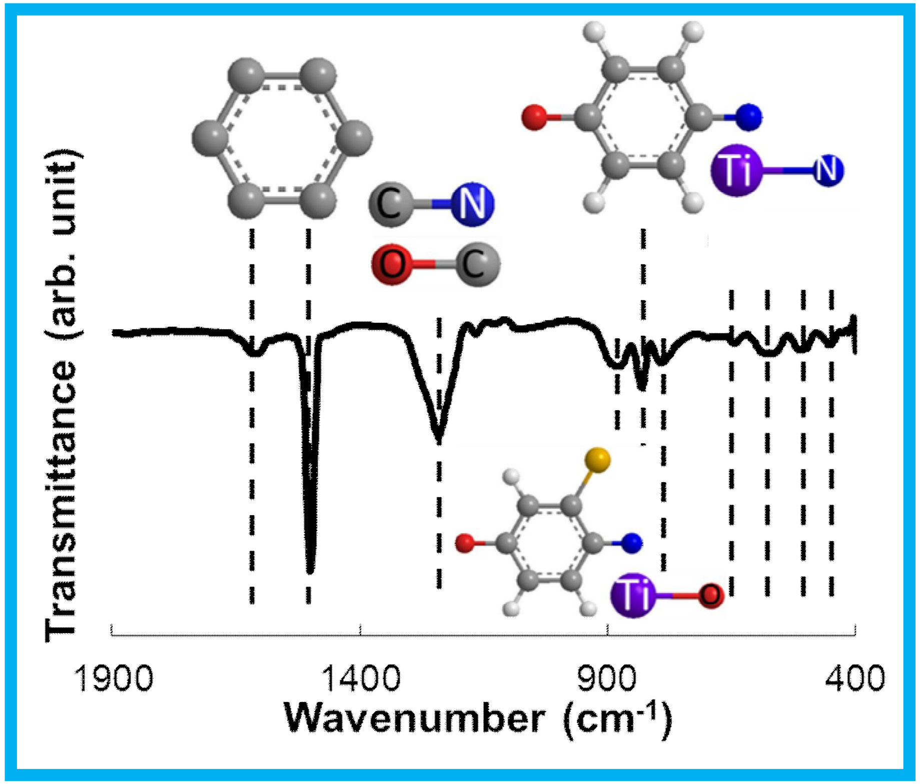


$TiCl_4$ + Aminophenol

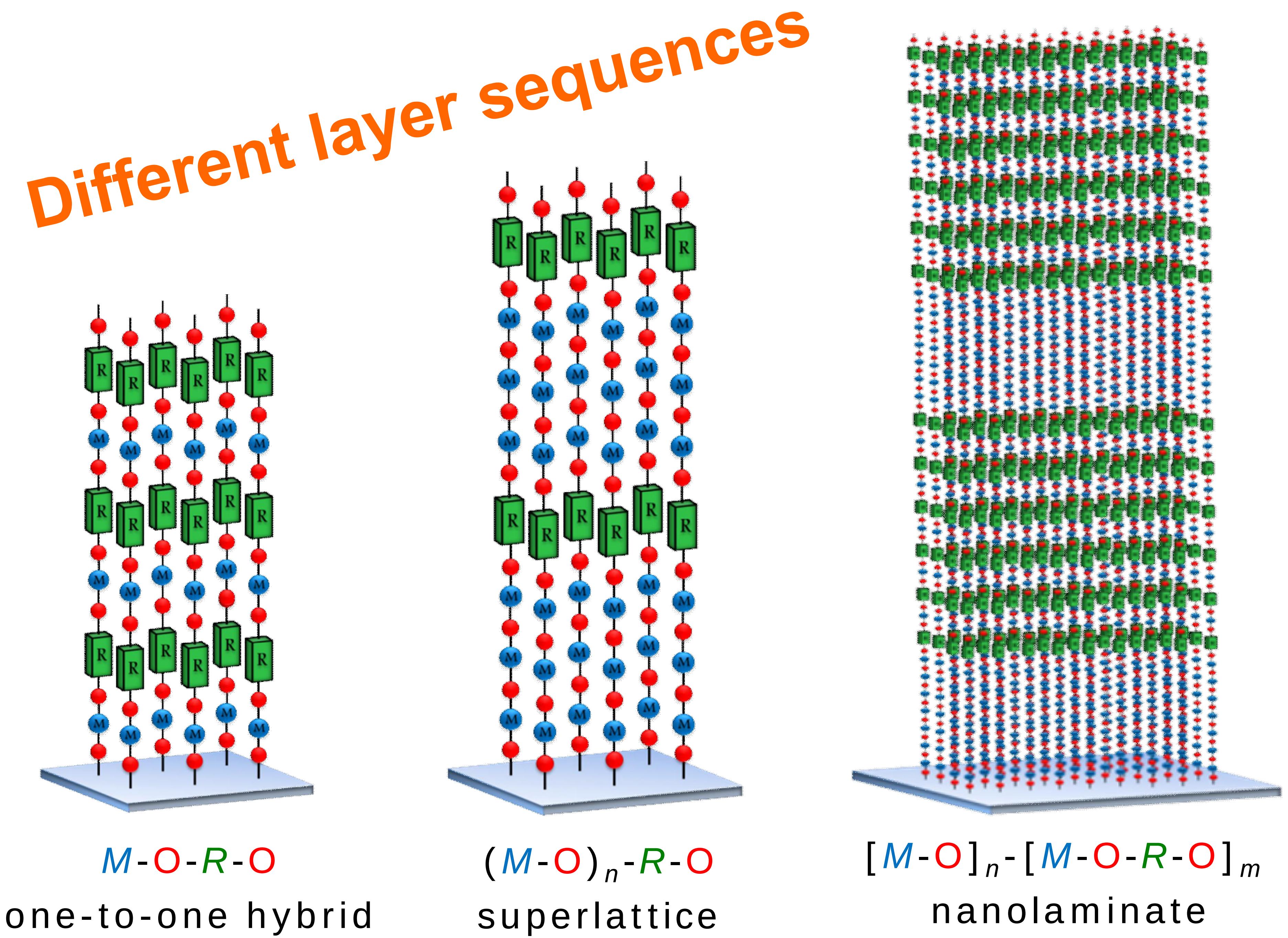




FTIR



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).


Different layer sequences
R
M
M-O-R-O
one-to-one hybrid
(M-O)$_n$-R-O
superlattice
[M-O]$_n$-[M-O-R-O]$_m$
nanolaminate

POSSIBLE APPLICATIONS OF ALD/MLD HYBRIDS …

- **GAS-BARRIER COATINGS**

  Al_2O_3 + alucone nanolaminate coatings on biopolymers:
  → **Enhanced mechanical (under strain) & thereby oxygen-gas barrier properties**

- **FLEXIBLE LUMINESCENCE MATERIALS**

  Ln + e.g. Pyridinedicarboxylic acid
  → **Organic component sensitizes lanthanide luminescence**

- **FLEXIBLE THERMOELECTRIC MATERIALS**

  Thermoelectric oxide-organic superlattice structures in a scale of 1~10 nm
  → **Significantly suppressed lattice thermal conductivity**

- **FLEXIBLE TRANSPARENT Li-ION BATTERY MATERIALS**

  Li + terephtalic acid / hydroquinone → **Electrodes for organic Li-ion microbattery**

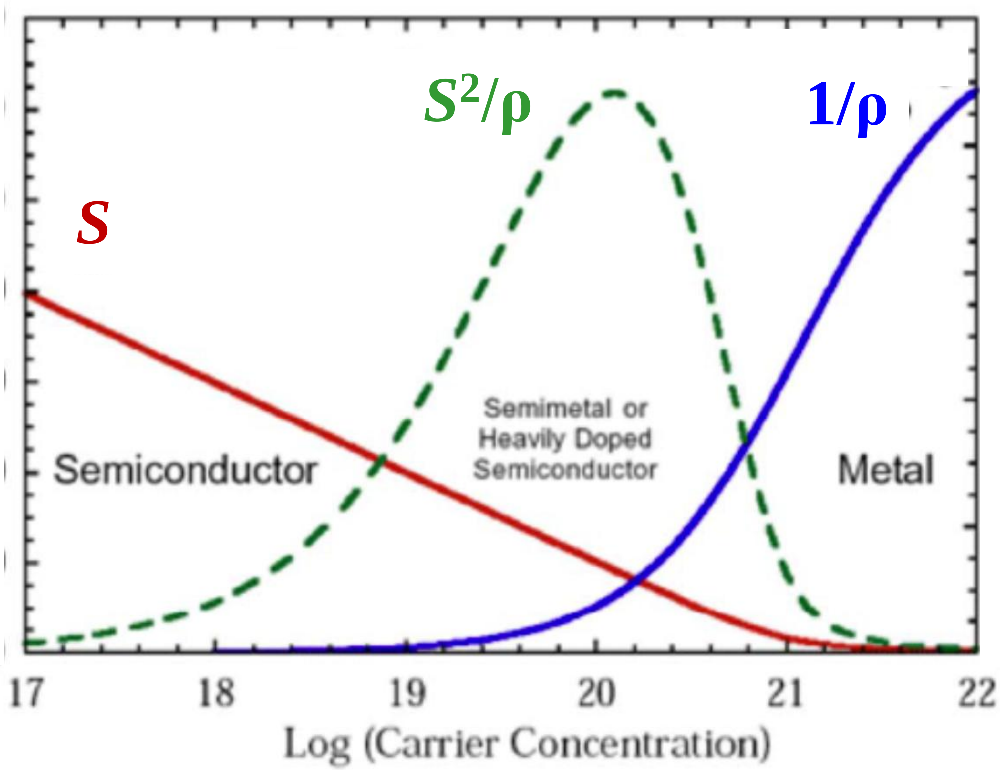
- **CRYSTALLINE INORGANIC-ORGANIC COORDINATION NETWORKS**

  Cu, Ca, … + terephtalic acid → **Crystalline MOF-type structures**

- **NEW EXCITING ORGANIC COMPONENTS …**

  Na + uracil
  → **novel 3D crystalline nucleobase structures with alkali metal linkers**

THERMOELECTRICS



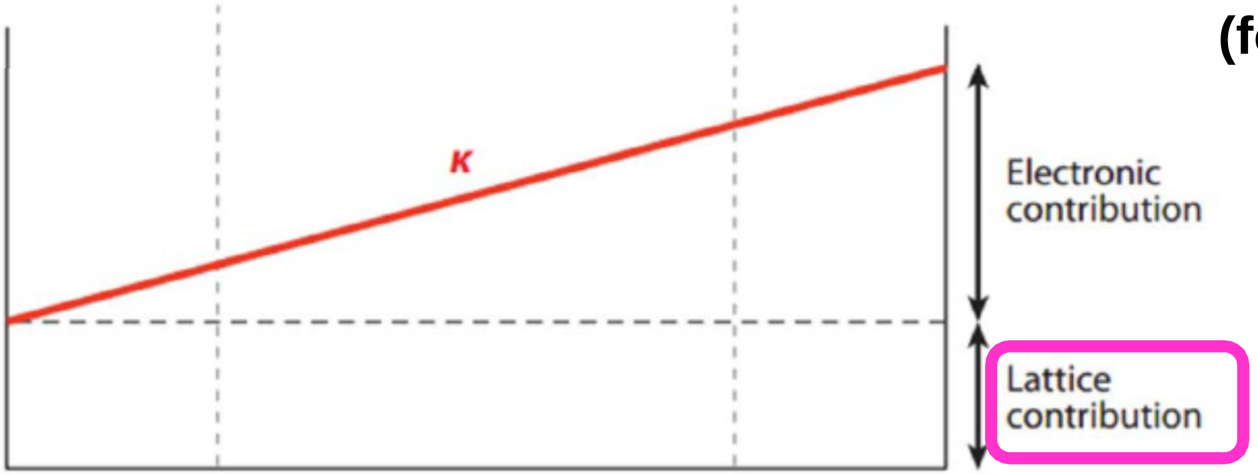


Figure-of-Merit

$$ZT = \frac{S^2}{\rho\kappa} T = \frac{S^2}{\rho(\kappa_e + \kappa_l)} T$$

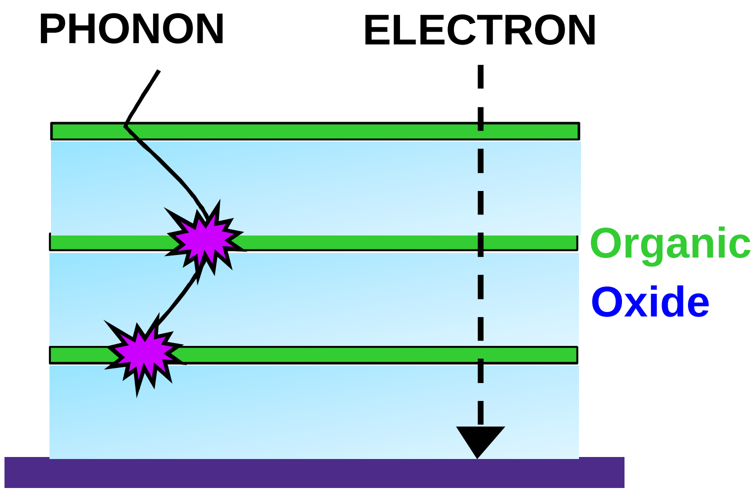
S: Seebeck constant
r : electrical resistivity
k: thermal conductivity

NANOSTRUCTURING

(for oxides κ_l large !)

OUR ALD/MLD APPROACH to TE oxide thin films

- **Superlattice: thermoelectric oxide layers & organic layers in a scale of 1 ~ 10 nm to block phonons without affecting electrons**
- **First proof-of-concept data: ZnO:benzene**
- **Massive reduction in thermal conductivity: 43 → 0.7 W m^{-1} K^{-1}**



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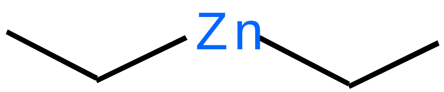
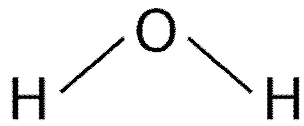
T. Tynell, A. Giri, J. Gaskins, P.E. Hopkins, P. Mele, K. Miyazaki & M. Karppinen, Efficiently suppressed thermal conductivity in ZnO thin films via periodic introduction of organic layers, ***J. Mater. Chem. A* 2**, 12150 (2014).

ALD/MLD for ZnO : Benzene superlattice

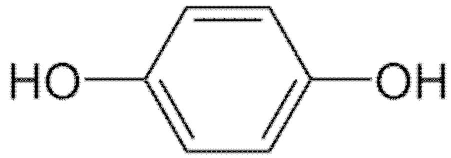
$Zn(CH_2CH_3)_2$



Water

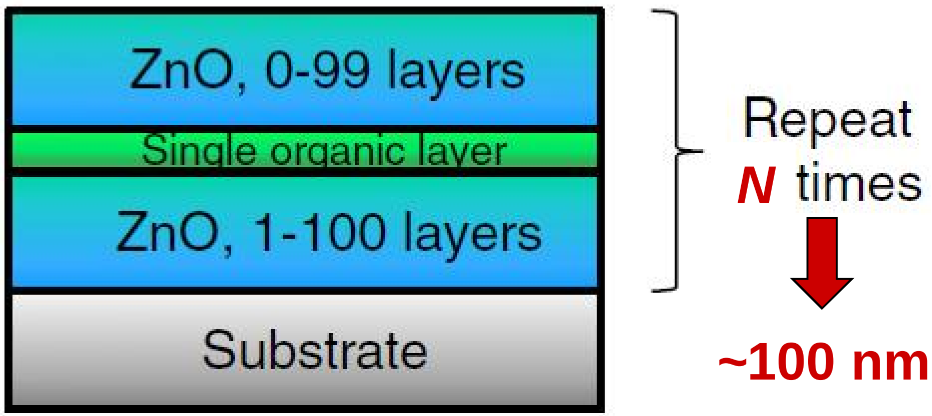


HQ: Hydroquinone

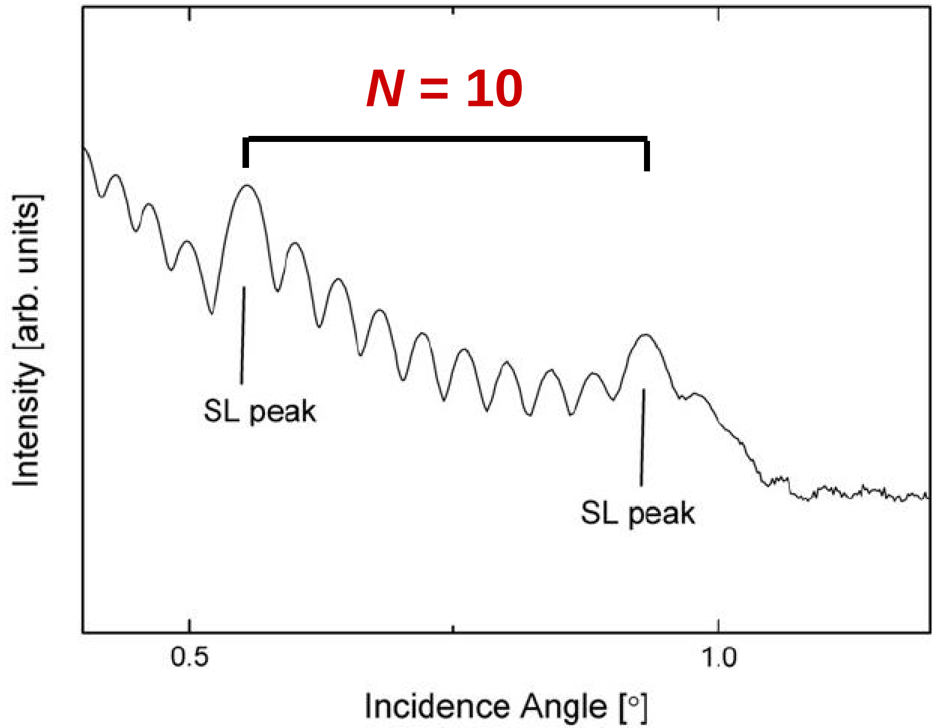


DEPOSITIONS

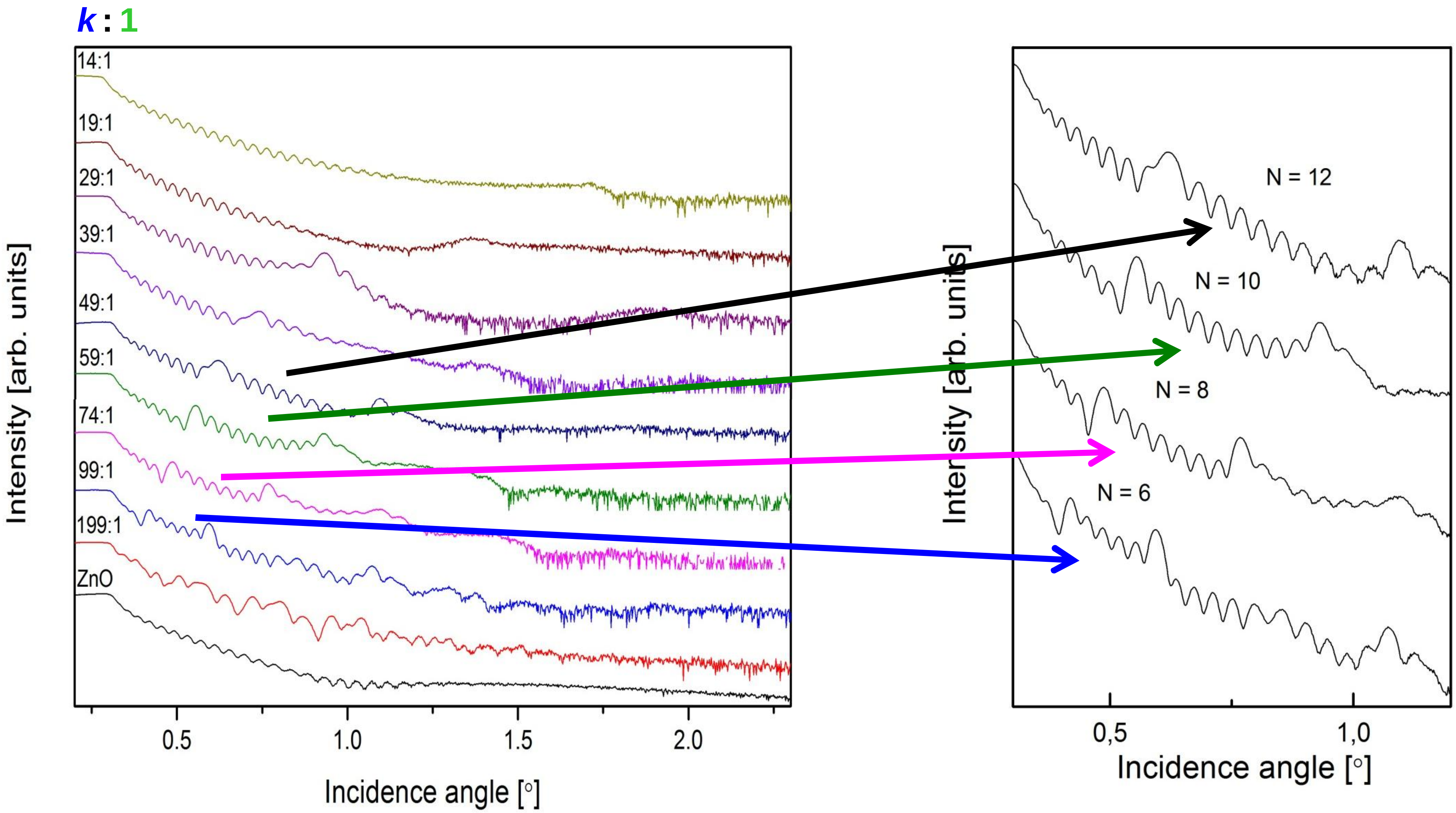
- 220 °C
- 600 ALD/MLD cycles in total



XRR: X-ray Reflectivity



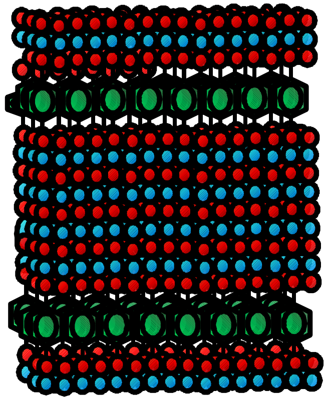
XRR: Clear evidence of the superlattice structure

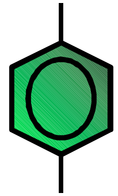


T. Tynell, I. Terasaki, H. Yamauchi & M. Karppinen, *Journal of Materials Chemistry A* **1**, 13619 (2013).

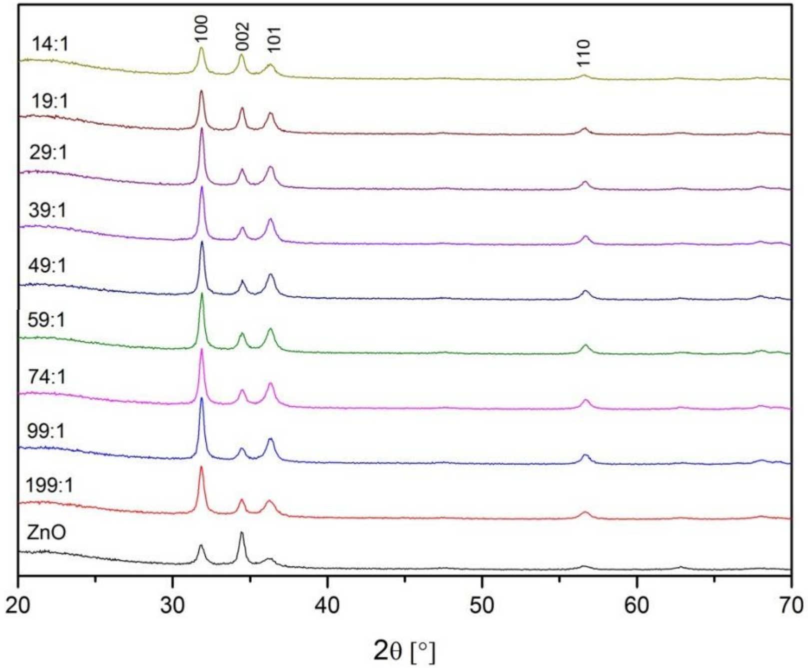
ALD : MLD

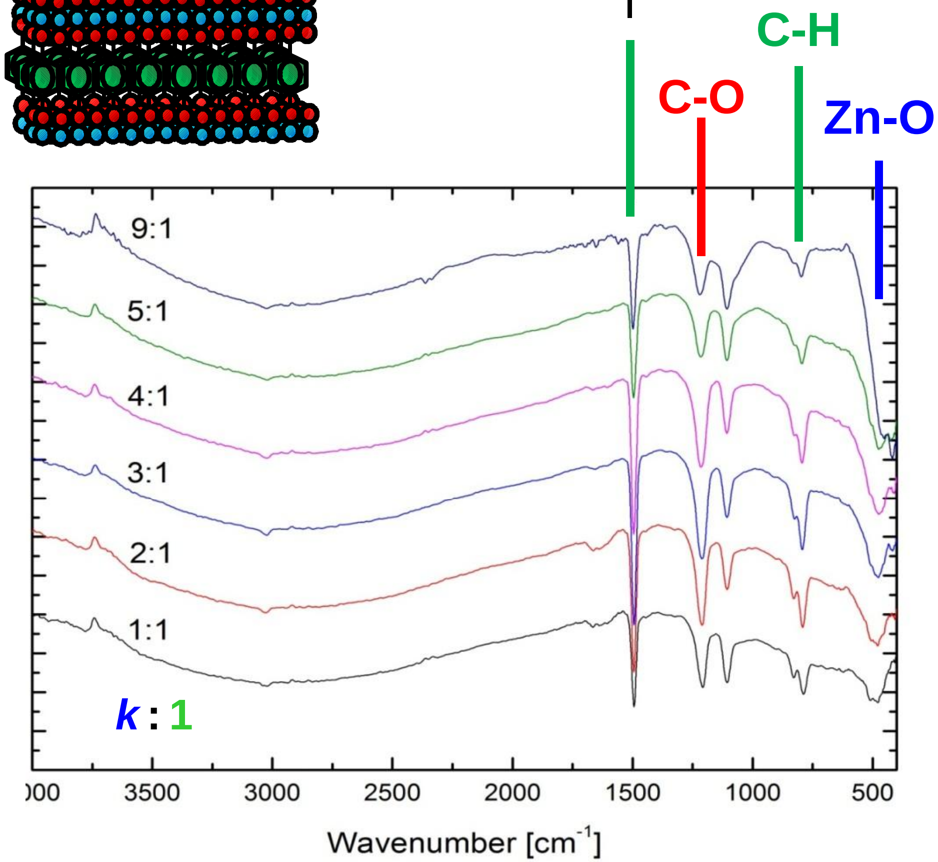
ZnO : HQ = *k* : 1





k : 1





GIXRD:

ZnO wurtzite structure,

no changes in crystallinity

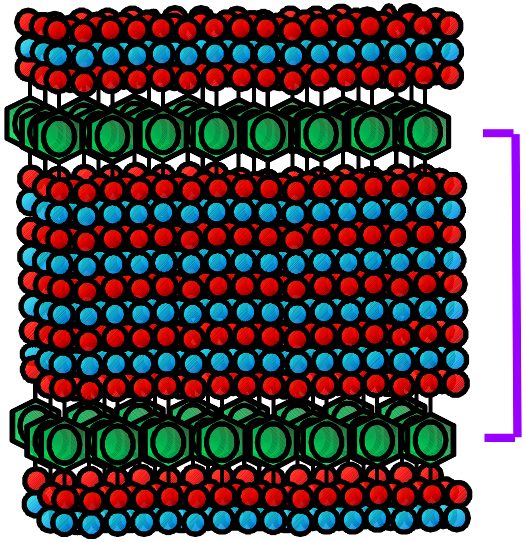
FTIR:

Presence of organic groups/bonds

anticipated for the ZnO:HQ films

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

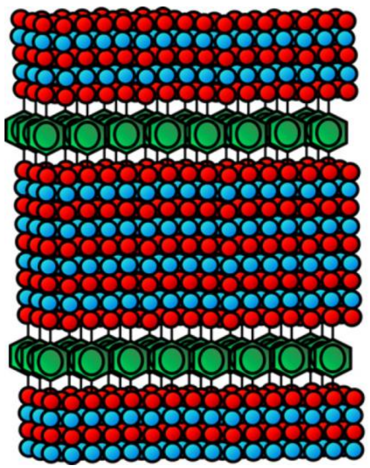
THERMAL CONDUCTIVITY (at RT)

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
49 : 1	
ZnO : 1 x benzene	4.1
ZnO : 3 x (ZnO-benzene)	3.2
ZnO : 5 x (ZnO-benzene)	2.4
ZnO : 7 x (ZnO-benzene)	1.9

IMPORTANTLY

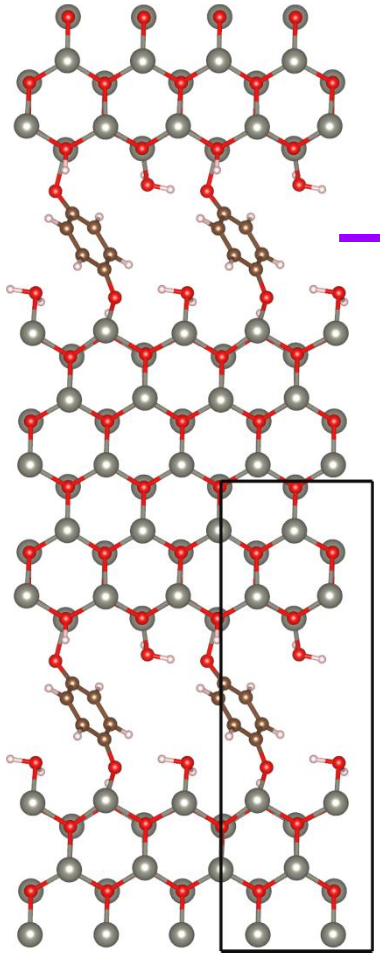
- Thickness of hybrid layer increases → from ballistic to diffusive heat transfer
- Proper Al-doping → electrical transport properties not much affected by the organic layers
- Superlattice structure remains stable upon heating in air up to 500-600 ^{o}C

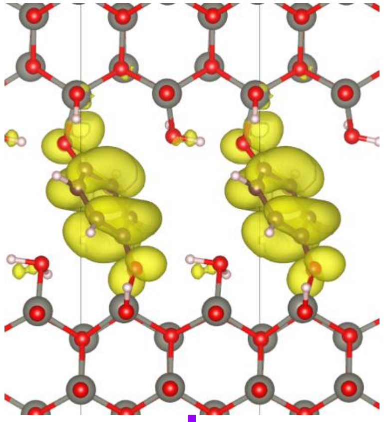
- T. Tynell, A. Giri, J. Gaskins, P.E. Hopkins, P. Mele, K. Miyazaki & M. Karppinen, ***J. Mater. Chem. A*** **2**, 12150 (2014).
- A. Giri, J.-P. Niemelä, C.J. Szwejkowski, M. Karppinen & P.E. Hopkins, ***Phys. Rev. B*** **93**, 024201 (2016).
- A. Giri, J.-P. Niemelä, T. Tynell, J. Gaskins, B.F. Donovan,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

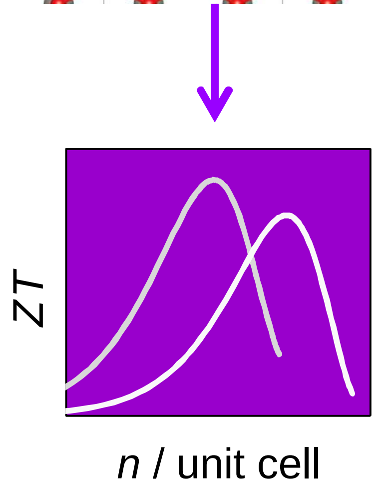


MODELLING

- **Computational** first-principles calculations
- **Atomic-level models** for Zn:HQ superlattices (surface coverage & chemical bonding at the interface)
- **Band structures** for Zn:HQ superlattices
- **Prediction of thermoelectric properties** (in line with experiments)
- **Systematic screening** of the properties of ZnO:organic superlattices for various organic constituents







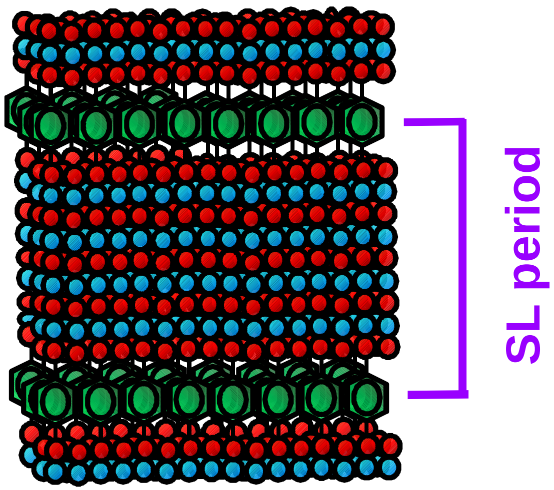
A.J. Karttunen, T. Tynell & M. Karppinen:

- *J. Phys. Chem. C* **119**, 13105 (2015).
- *Nano Energy* **22**, 338 (2016).

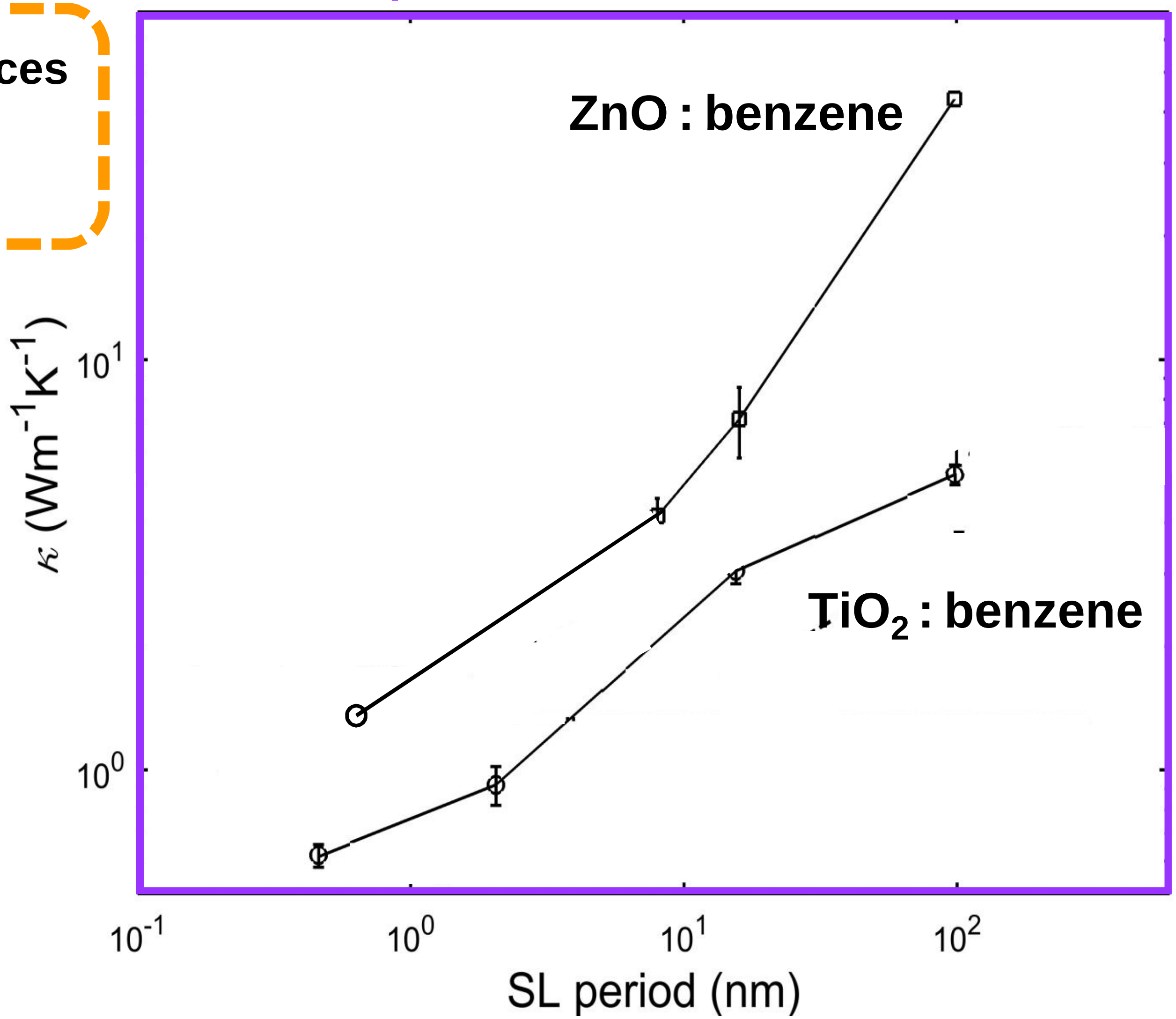
HOW ABOUT OTHER SYSTEMS: TiO_2 ?

TiO_2:benzene superlattices

- § $TiCl_4$ + H_2O + HQ
- § Deposition at 210 ºC



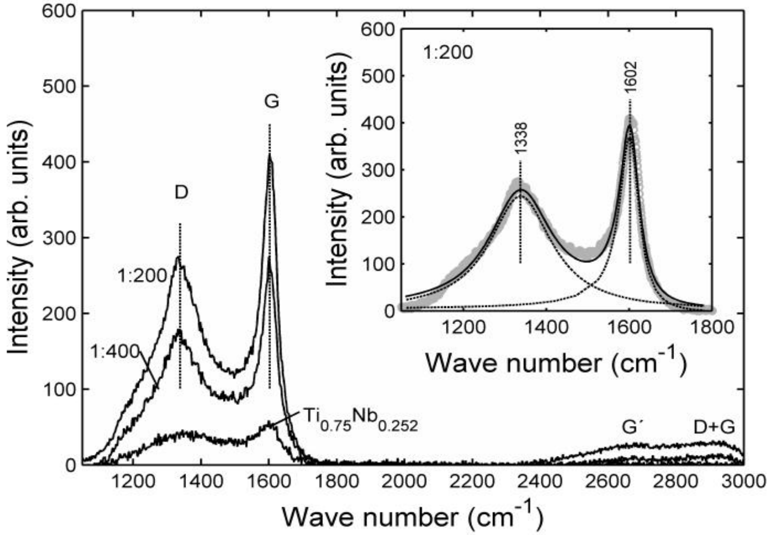
Room-Temperature THERMAL CONDUCTIVITY



J.-P. Niemelä, A.J. Karttunen & M. Karppinen, *J. Mater. Chem. C* **3**, 10349 (2015).

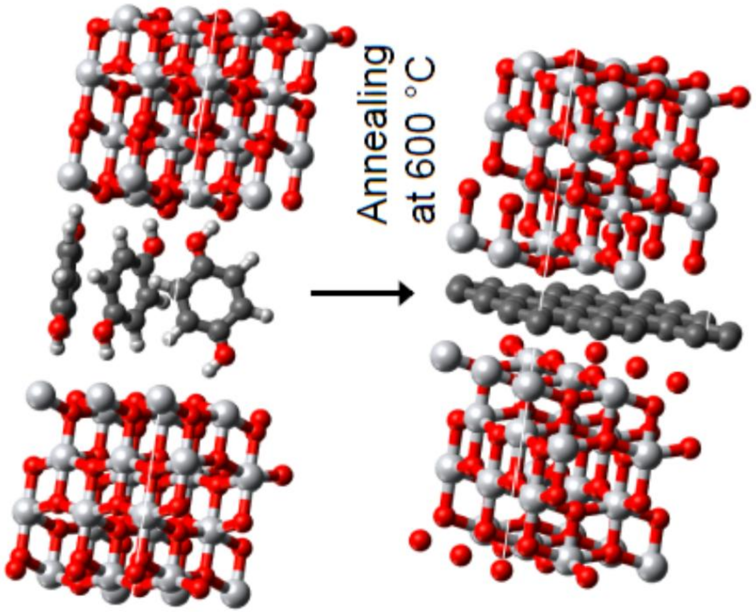
TiO_2-based superlattices

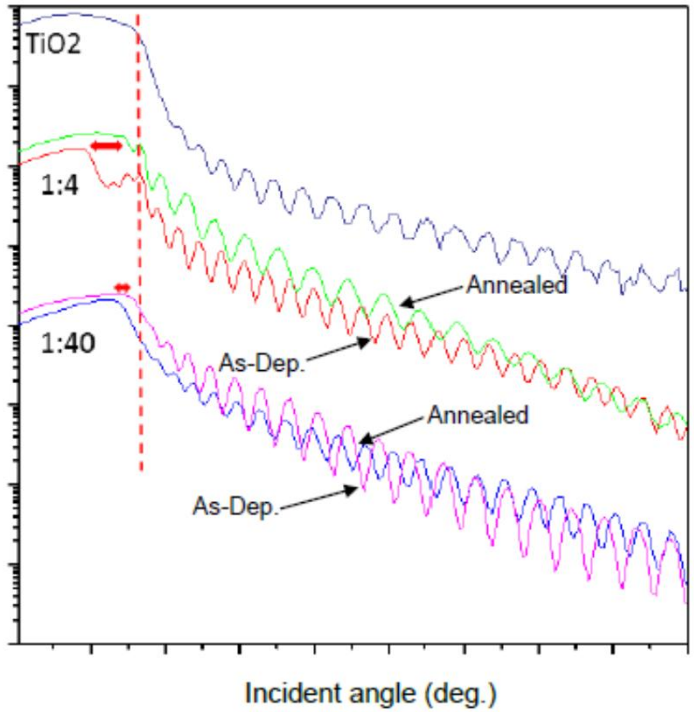
- $TiCl_4$ + H_2O + HQ
- Deposition at 210 ºC
- Annealing in H_2/Ar at 600 ºC



UPON ANNEALING

- FTIR: NO benzene
- Raman: graphitic-type carbon
- XRR: superlattice remains
- XRR: density increases

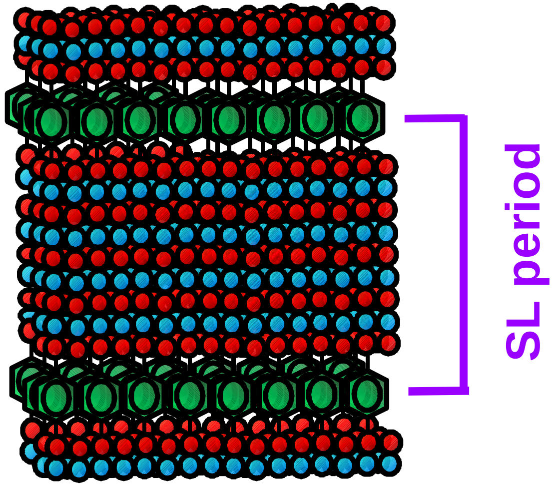


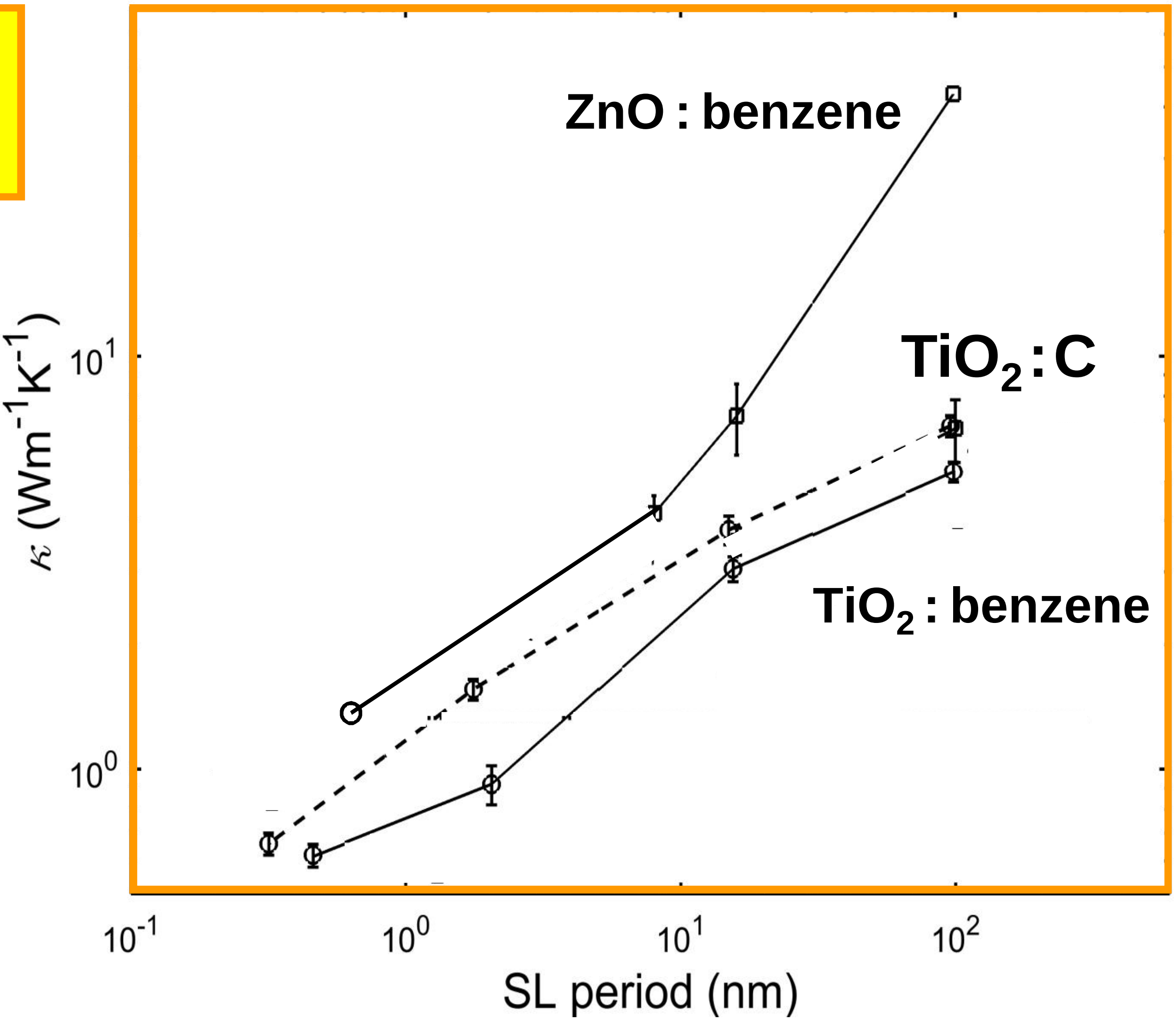


Niemelä, Giri, Hopkins & Karppinen, *J. Mater. Chem. A* **3**, 11527 (2015).

ROOM-TEMPERATURE THERMAL CONDUCTIVITY DATA

Measured by TDTR
(Time-Domain ThermoReflectance)
by prof. Patrick Hopkins
at University of Virginia

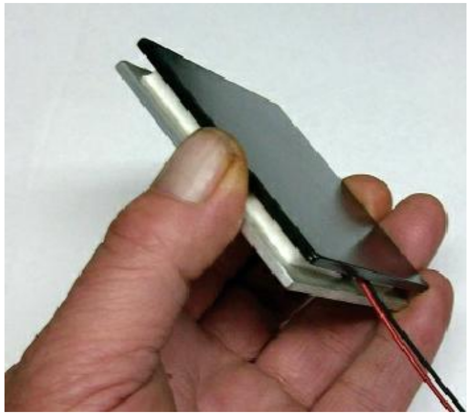




J.-P. Niemelä, A.J. Karttunen & M. Karppinen, *J. Mater. Chem. C* **3**, 10349 (2015).

Novel Thermoelectric Energy Solutions

OXIDE:ORGANIC SUPERLATTICE thin-film thermoelectrics by ALD/MLD for ENHANCED PERFORMANCE



From current "bulky" thermoelectric devices...

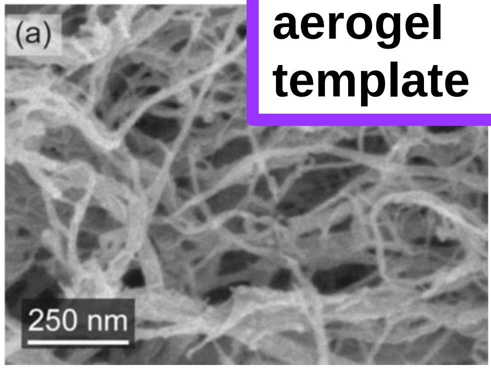
... to flexible, thin-film thermoelectric devices…

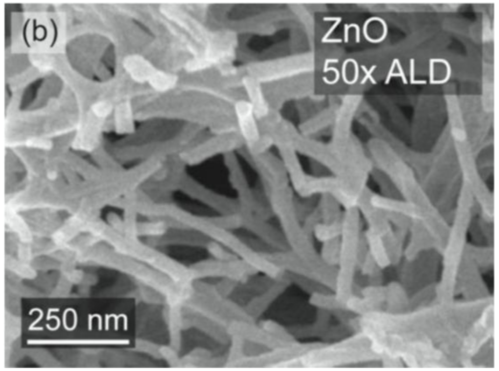
…enabling integrated energy solutions for textiles, polymers, ...

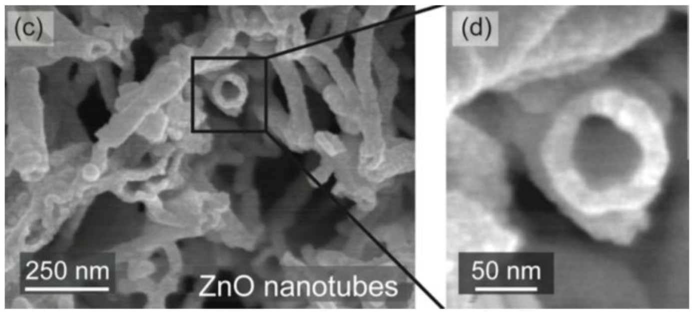
FUTURE VISION
Flexible/wearable devices enabling heat harvesting in everyday life

Korhonen, Malm, Karppinen, Ikkala & Ras, *ACS Nano* 5, 1967 (2011).

Freeze-dried nanocellulose aerogel template





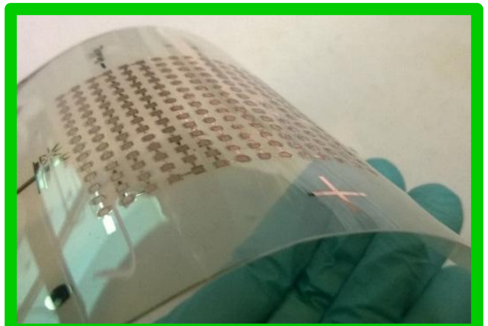


ALD/MLD coating

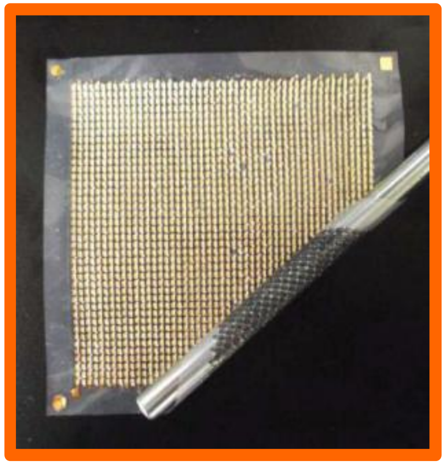
Calcination at ~400 °C

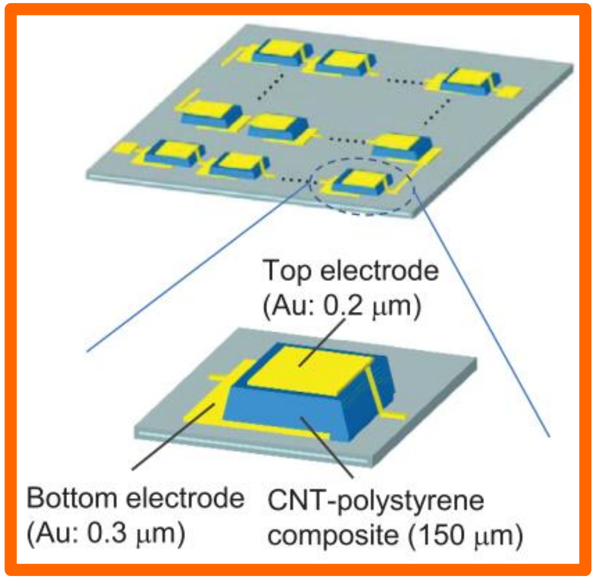
ZnO-benzene nanotubes

THERMOELECTRIC MODULE



OUR drop-casted nanocellulose/ALD-ZnO

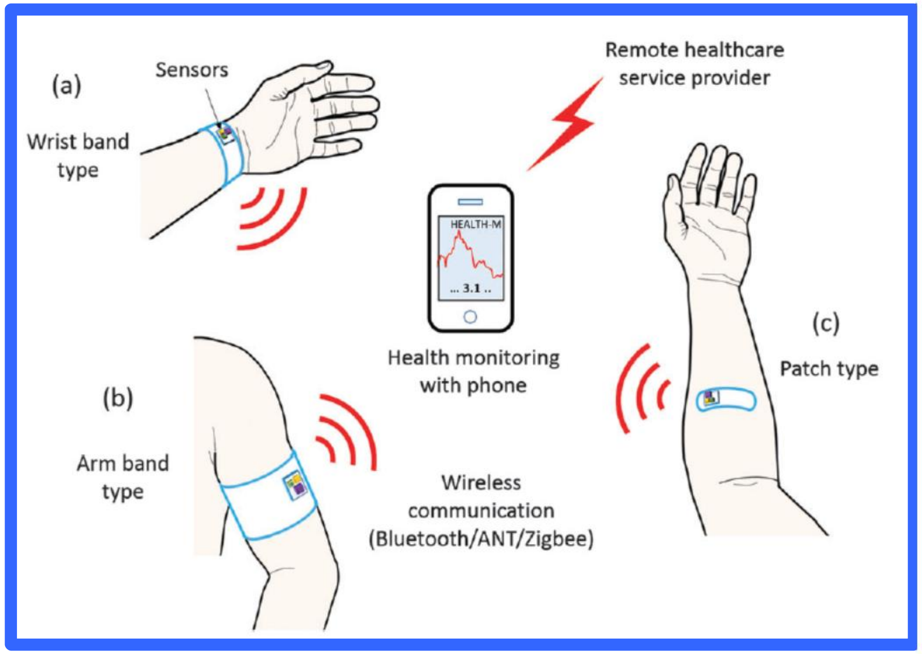


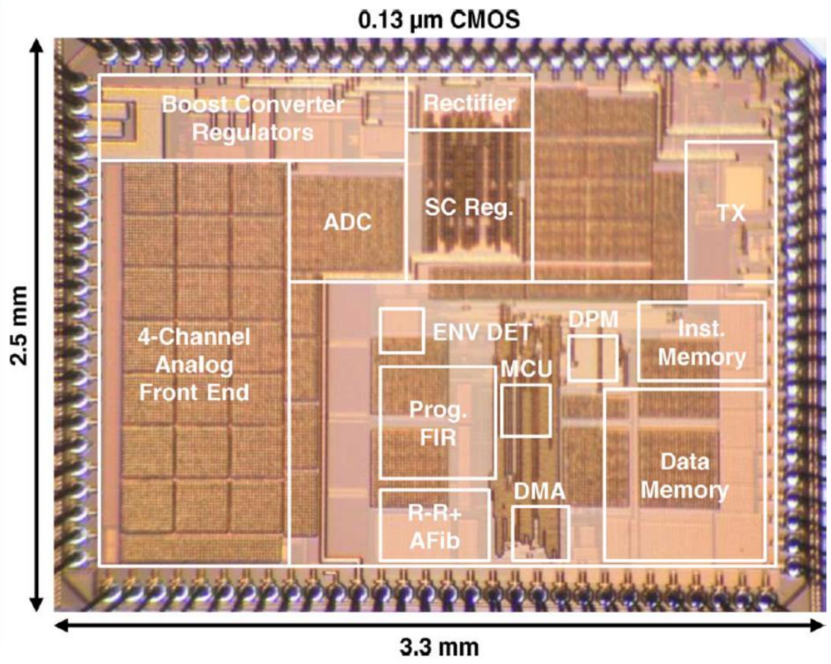


Mixing TE-CNT with polymer & printing on textile

Suemori et al., APL 103, 153902 (2013).

Only 19 µW is enough ?

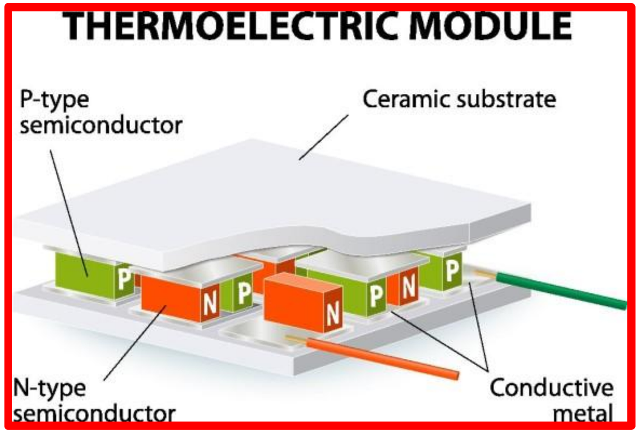




- J.-H. Bahk *et al.*, *J. Mater. Chem. C* **3** (2015).
- Y. Zhang *et al*., *IEEE J. Solid-State Circuits* **48** (2013).

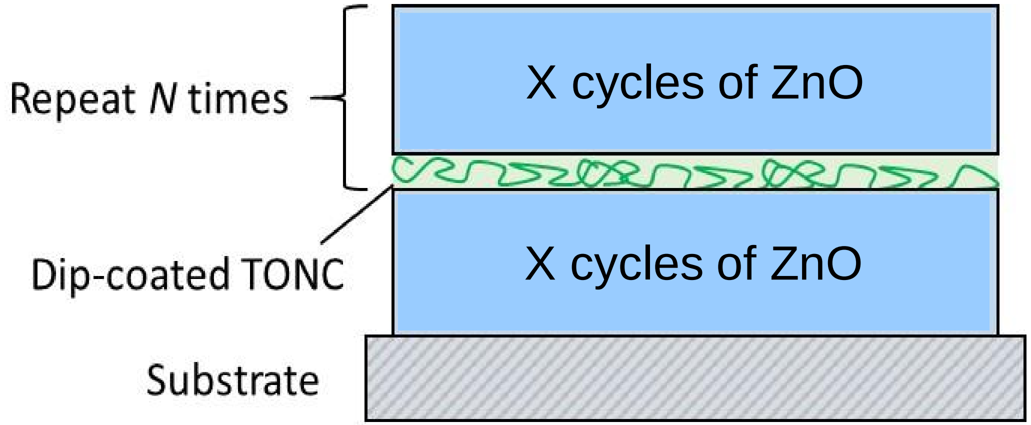
ALD thermoelectric oxide films (dep. 160 – 250 °C)

ROOM-TEMPERATURE TE CHARACTERISTICS



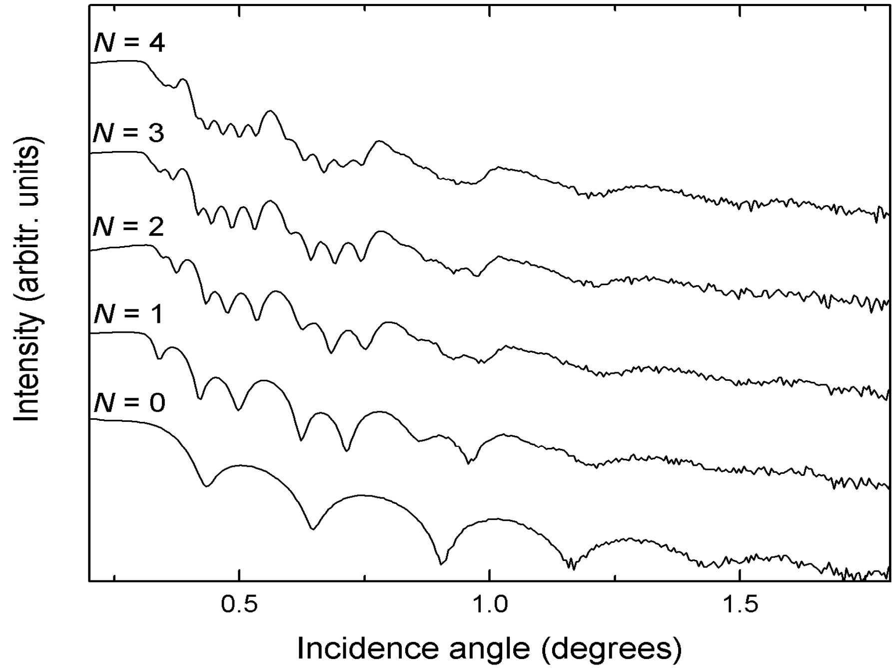
ALD thin film	Precursors	*S* [μV/K]	ρ [mΩ cm]
$(Zn_{0.98}Al_{0.02})O$	$Zn(CH_2CH_3)_2$, $Al(CH_3)_3$, H_2O	- 60	70
$(Ti_{0.75}Nb_{0.25})O_2$	$TiCl_4$, $Nb(OEt)_5$, H_2O	- 12	1.4
$[CoCa_2O_3]_{0.62}CoO_2$	$Ca(thd)_2$, $Co(thd)_2$, O_3	+ 115	10
$CuCr_2O_4$	$Cr(acac)_3$, $Cu(thd)_2$, O_3	+ 170	$4x10^3$
$CuCrO_2$	$Cr(acac)_3$, $Cu(thd)_2$, O_3	+ 350	10^3
$Cu(Cr_{0.97}Mg_{0.03})O_2$	$Cr(acac)_3$, $Mg(thd)_2$, $Cu(thd)_2$, O_3	+ 120	30
CuO	$Cu(acac)_2$, H_2O	+ 150	10^3
$NiCo_2O_4$	$Ni(tmhd)_2$, $Co(tmhd)_2$, O_3	+ 100	1

NanoCellulose?



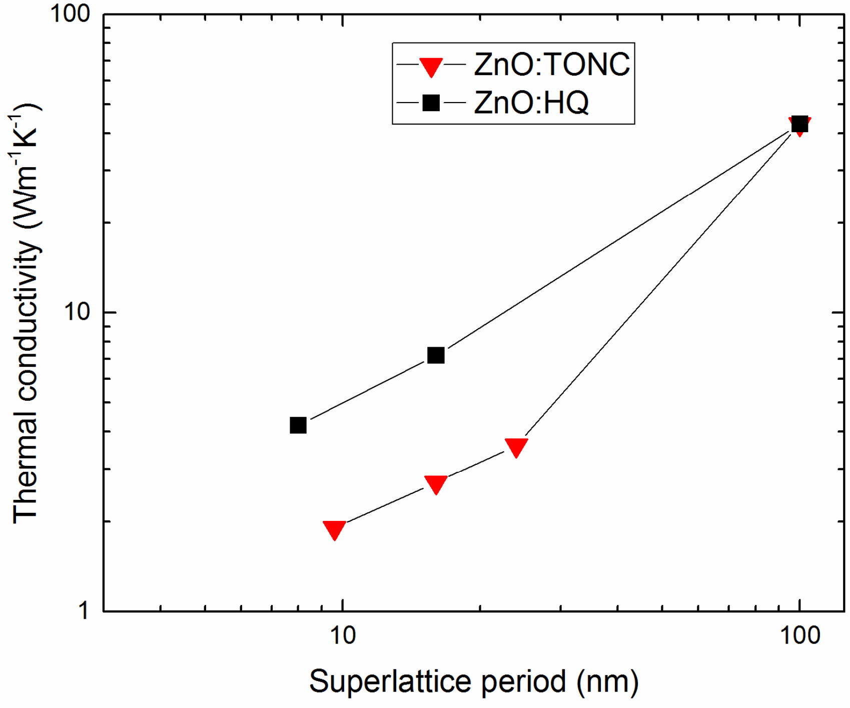
Monomolecular benzene-ring layers
→ Nanocellulose fibers

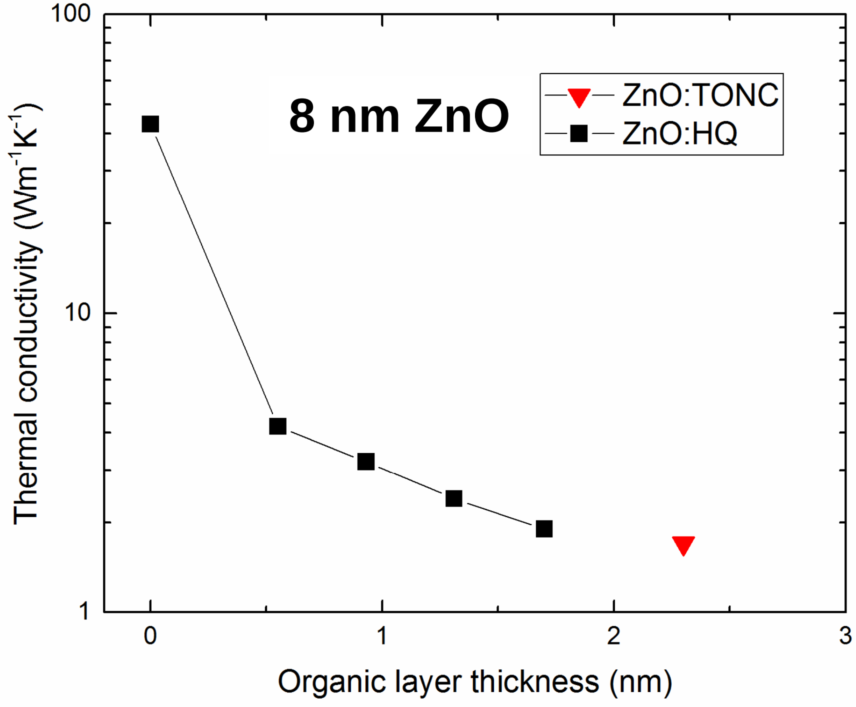
- **TONC:** TEMPO-oxidized nanocellulose
- **Dip-coating**
- 2-3 nm TONC layers
- Well-defined superlattice structures
- Remain stable in air up to ~450 °C



Ultralow thermal conductivity in hybrid ZnO:nanocellulose superlattice thin films
H. Jin, G. Marin, A.Giri, T. Tynell, M. Gestranius, B.P. Wilson,
E. Kontturi, T. Tammelin, P.E. Hopkins & M. Karppinen,
Journal of Materials Science, in press (2017).

Thermal Conductivity





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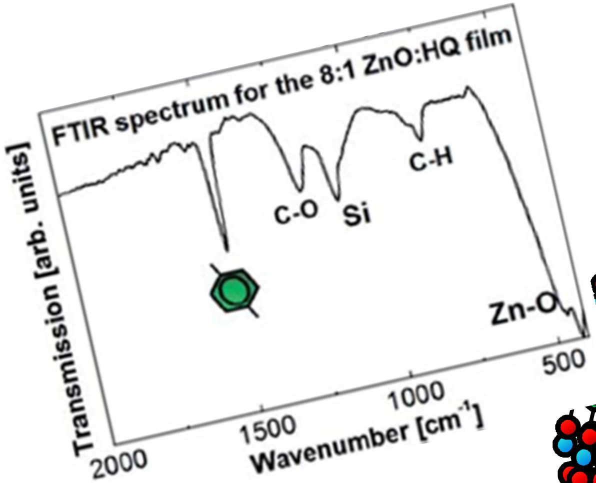
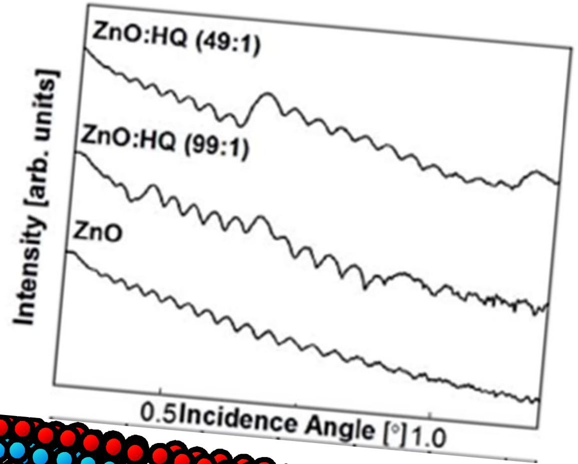
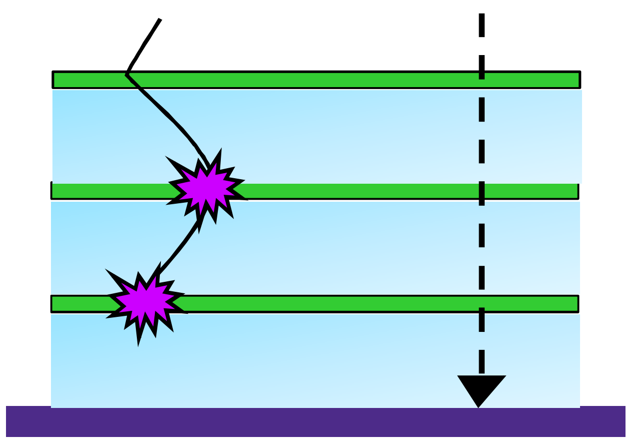
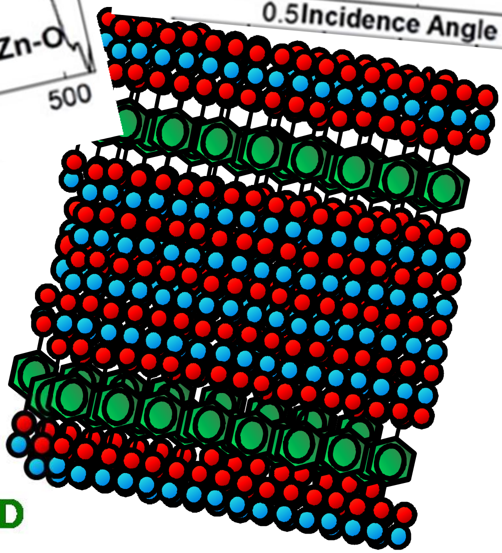
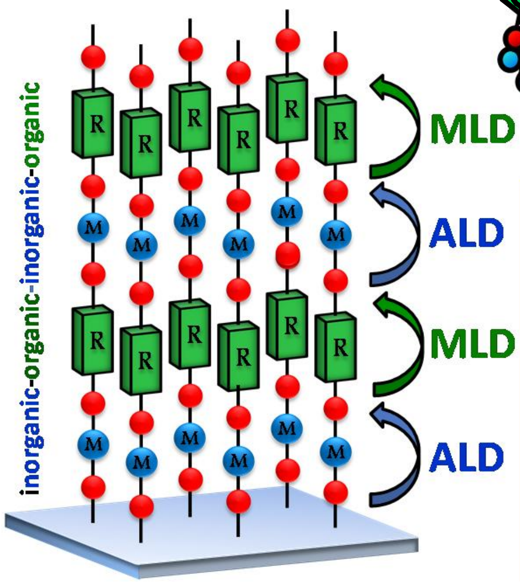








EXITING YES,
USABLE ?



- **Novel layer-engineered hybrid materials**
- **Enhanced thermoelectric characteristics**
- **Fabricated with industrially feasible ALD/MLD technique**
- **Mechanically flexible & thermally surprisingly stable**
- **Conformal → Possibility for further nanostructuring**
- **Novel material properties discovered & more expected !**