Spatial ALD research at LMGP

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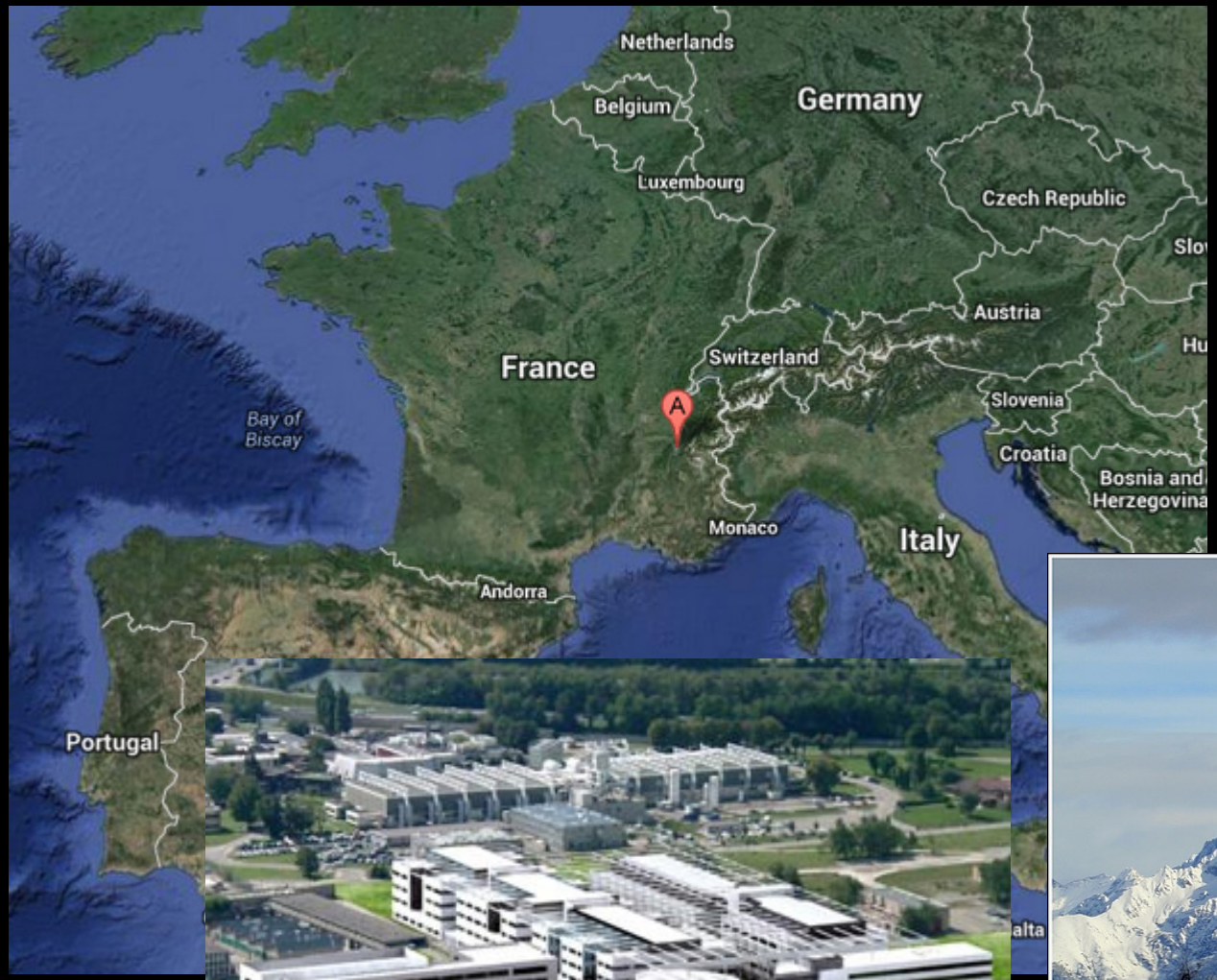
Laboratoire des Matériaux et du Génie Physique (Grenoble-INP/CNRS)

Spatial ALD day, TU/e, Eindhoven, The Netherlands

9th June 2022

Where are we?


Netherlands
Belgium
Germany
Luxembourg
Czech Republic
Austria
France
Switzerland
Slovenia
Croatia
Bosnia and Herzegovina
Monaco
Italy
Andorra
Portugal
Bay of Biscay
A


LMGP

Thanks to the SALD Team!

Acknowledgements

- *FUNDING*

Eco-SESA Université Grenoble Alpes

CONACYT

UGA Université Grenoble Alpes

anr

INSTITUT CARNOT Energies du futur

MARIE CURIE ACTIONS

SPRINT

cnrs

arc COMMUNAUTÉS DE RECHERCHE ACADÉMIQUE RhôneAlpes ENERGIES

CEMAM Laboratoire d'excellence

HYSTORE

EPISTORE ENERGY IN THIN LAYERS

- *COLLABORATORS*

ANNEALSYS

IMEP-LAHC

SIMAP

PHENIKAA UNIVERSITY

ines INSTITUT NATIONAL DE L'ENERGIE SOLAIRE

INMA INSTITUTO DE NANOCIENCIA Y MATERIALES DE ARAGÓN

cea

LTM LABORATOIRE DES TECHNOLOGIES DE LA MICROÉLECTRONIQUE

Imperial College London

GREMI

UNIVERSITY OF WATERLOO CONCORDIA CUM VERITATE

RUB

iem

First SALD patents and publications

Patented 1977, Suntola et al.

United States Patent [19]

Suntola et al.

[11] 4,058,430

[45] Nov. 15, 1977

[54] **METHOD FOR PRODUCING COMPOUND THIN FILMS**

[76] Inventors: **Tuomo Suntola**, Riihikallio, 02610 Espoo 61, Finland; **Jorma Antson**, Urheilutie 22, 01350, Vantaa 35, Finland

[21] Appl. No.: **635,233**

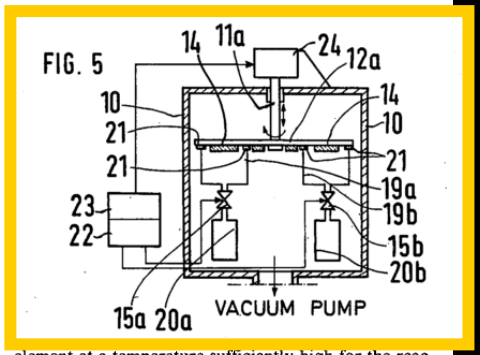
[22] Filed: **Nov. 25, 1975**

[30] **Foreign Application Priority Data**

Nov. 29, 1974 Finland 743473

[51] **Int. Cl.**[2] **B05D 5/00**; B05D 5/12

[52] U.S. Cl. 156/611; 118/49;



element at a temperature sufficiently high for the reac-

United States Patent [19]

Suntola et al.

[11] **4,389,973**

[45] **Jun. 28, 1983**

[54] **APPARATUS FOR PERFORMING GROWTH OF COMPOUND THIN FILMS**

[75] Inventors: **Tuomo S. Suntola; Arto J. Pakkala; Sven G. Lindfors**, all of Espoo, Finland

[73] Assignee: Oy Lohja AB, Virkkala, Finland

[21]

[56] **References Cited**

U.S. PATENT DOCUMENTS

3,602,192	8/1971	Grockowski	118/719
3,721,583	3/1973	Blakeslee	156/611
3,825,439	7/1974	Tick	427/93 X
3,964,937	6/1976	Post et al.	427/255.7 X
4,015,558	4/1977	Small et al.	118/719 X
			118/719

SALD at Atm. Pressure, no vaccum

APPLIED PHYSICS LETTERS **92**, 19210 (2008)

Stable ZnO thin film transistors by fast open air atomic layer deposition

David H. Levy,[a] Diane Freeman, Shelby F. Nelson, Peter J. Cowdery-Corvan, and Lyn M. Irving
Research Laboratories, Eastman Kodak Company, Rochester, New York 14650-2102, USA

Kodak

(Received 2 April 2008; accepted 17 April 2008; published online 12 May 2008)

We report stable, high performance zinc oxide thin film transistors grown by an pressure atomic layer deposition system. With all deposition and processing steps kept at or below 200 °C, the alumina gate dielectric shows low leakage (below 10^{-8} A/cm^2) and high breakdown fields. Zinc oxide thin film transistors in a bottom gate geometry yield on/off ratios above 10^8, near zero turn-on voltage, little or no hysteresis, and mobility greater than 10 cm^2/V s. With alumina passivation, shifts in threshold voltage under gate bias stress compare favorably to those reported in the literature. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2924768]

APPLIED PHYSICS LETTERS **93**, 172111 (2008)

Reproducible growth of *p*-type ZnO:N using a modified atomic layer deposition process combined with dark annealing

L. Dunlop,[a] A. Kursumovic, and J. L. MacManus-Driscoll
Department of Materials Science, University of Cambridge, Pembroke St., Cambridge CB United Kingdom

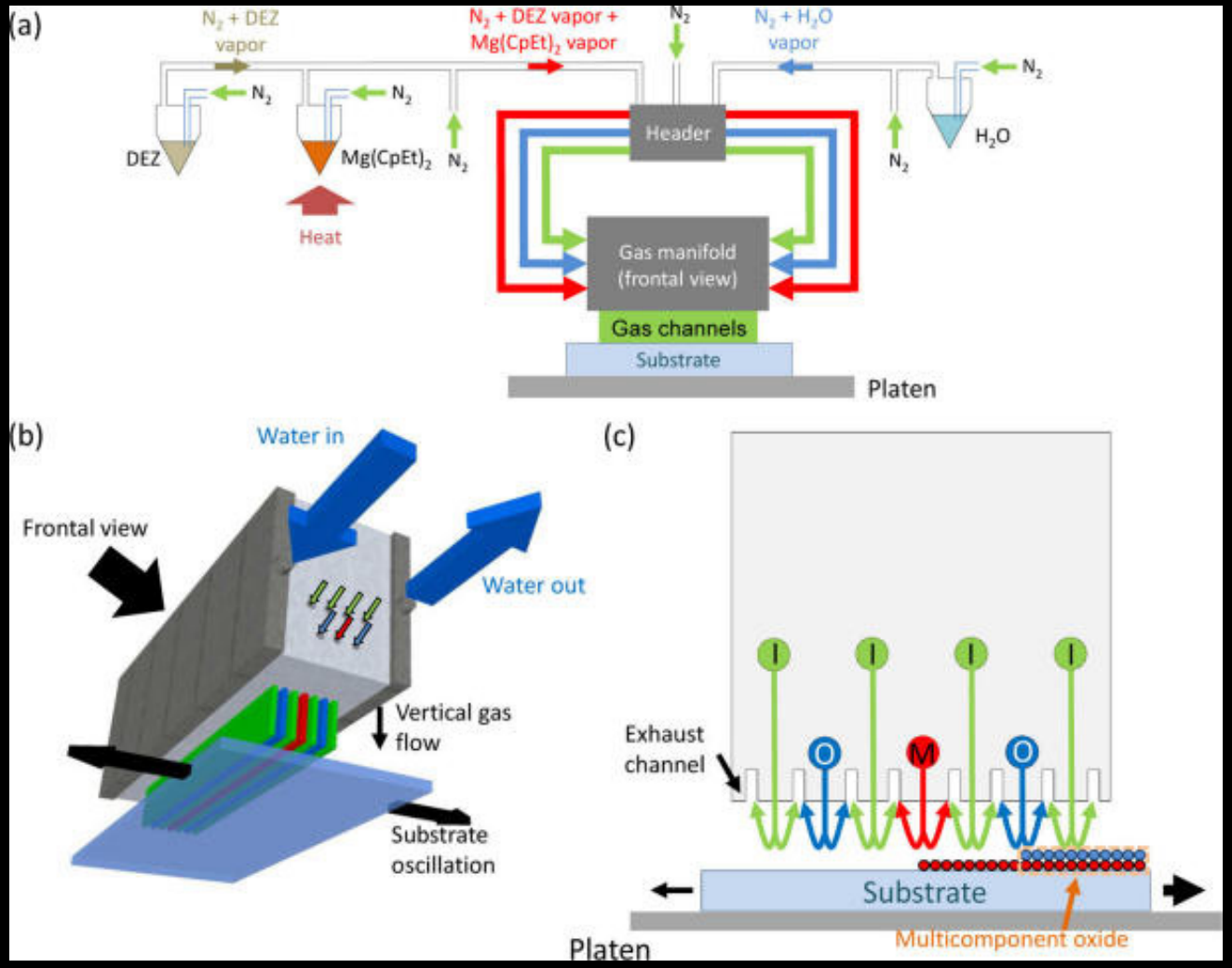
Kodak

(Received 8 July 2008; accepted 16 September 2008; published online 31 Octob

Nitrogen doped ZnO (ZnO:N) films were deposited by atmospheric atomic layer deposition (ALD) between 100 and 300 °C. Postannealing was required to remove compensating defects. temperature dark annealing, originally *n*-type films became *p*-type. Films deposi temperatures (≤150 °C) have low hole mobilities (μ) of 0.2–0.4 cm^2 V^{-1} s^{-1} and mc concentrations (n_p) of around 1×10^{15} cm^{-3}. Higher temperature deposited films (≥20 higher μ values (6 cm^2 V^{-1} s^{-1}) but n_p values $<1\times10^{13}$ cm^{-3}. This crossover i properties can be explained by the opposing effects of deposition temperature on nitrc level and distribution, and film crystallinity. © *2008 American Institute of Physics*. [DOI: 10.1063/1.3000604]

Open-air SALD @ LMGP

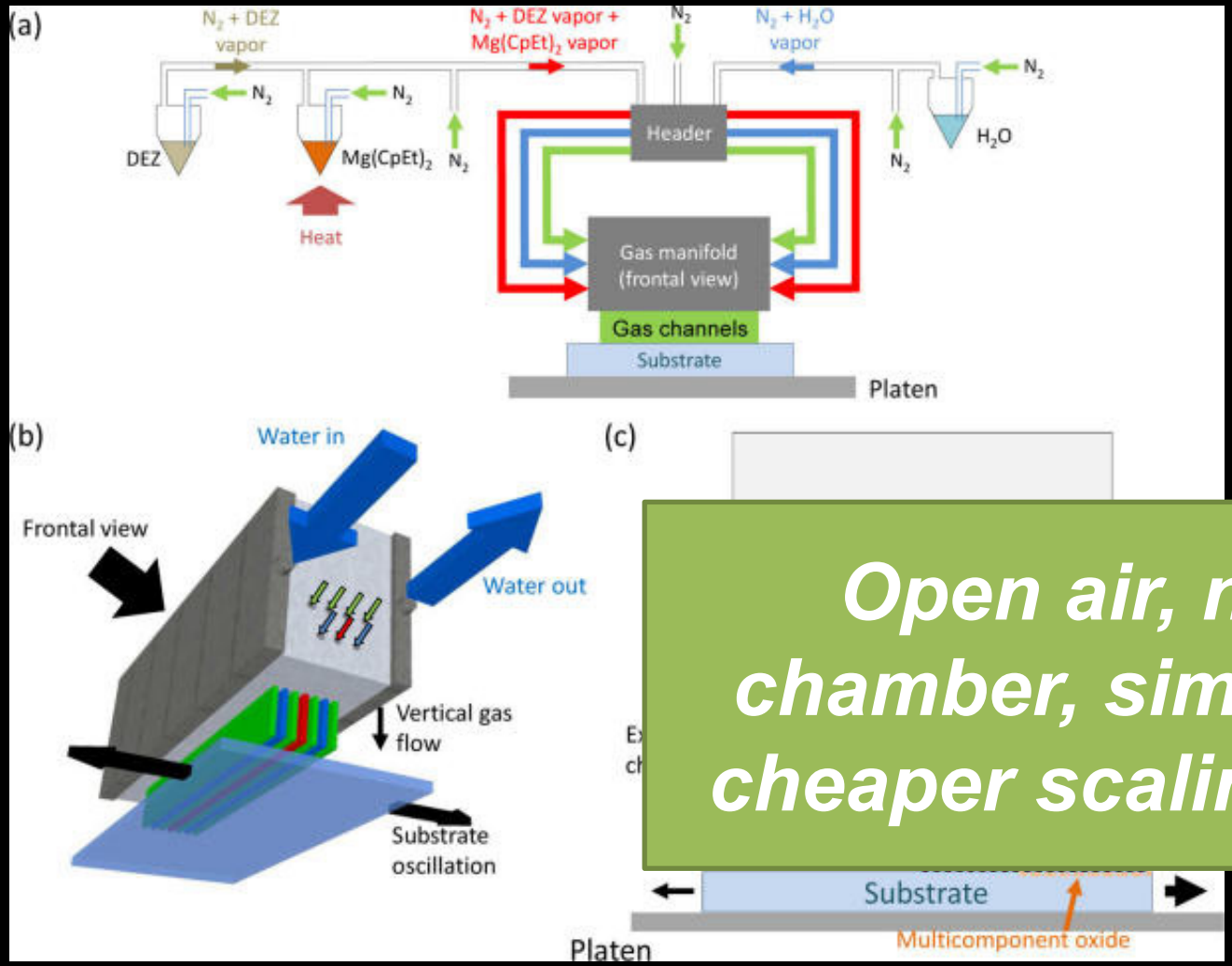
Based on a close-proximity, manifold injection head

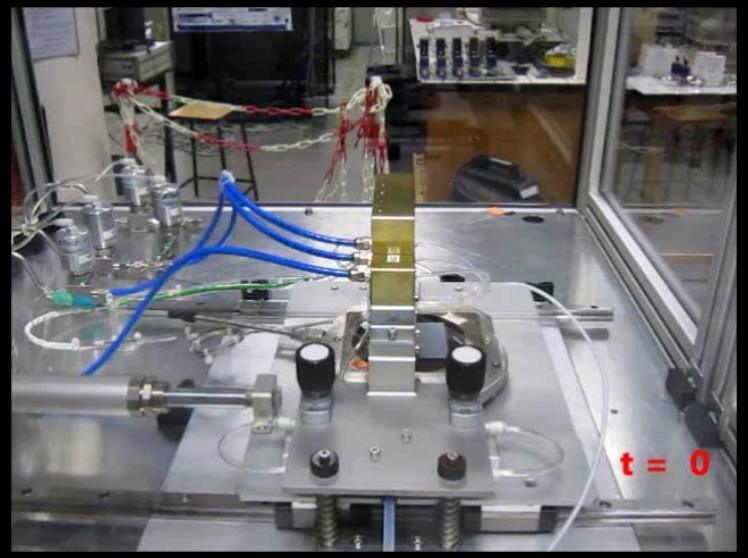


DMR, Mat. Horizons, 2014, 1, 314.

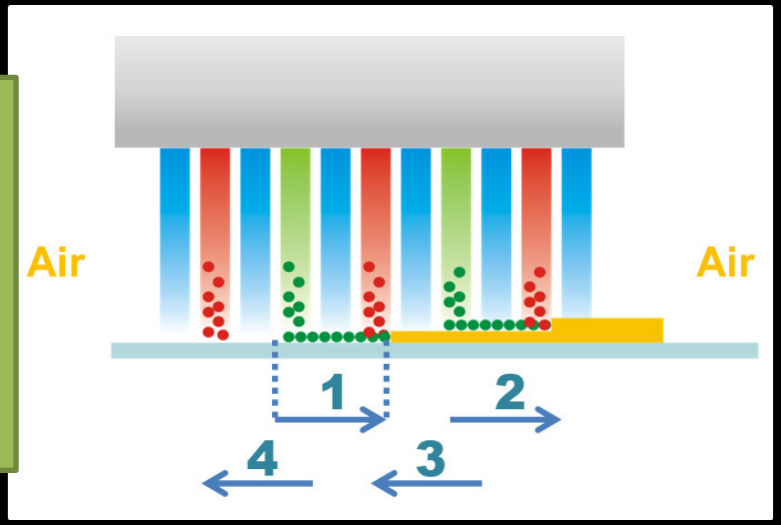
Open-air SALD @ LMGP

Based on a close-proximity, manifold injection head





Open air, no chamber, simpler, cheaper scaling up



DMR, Mat. Horizons, 2014, 1, 314.

Open-air SALD @ LMGP

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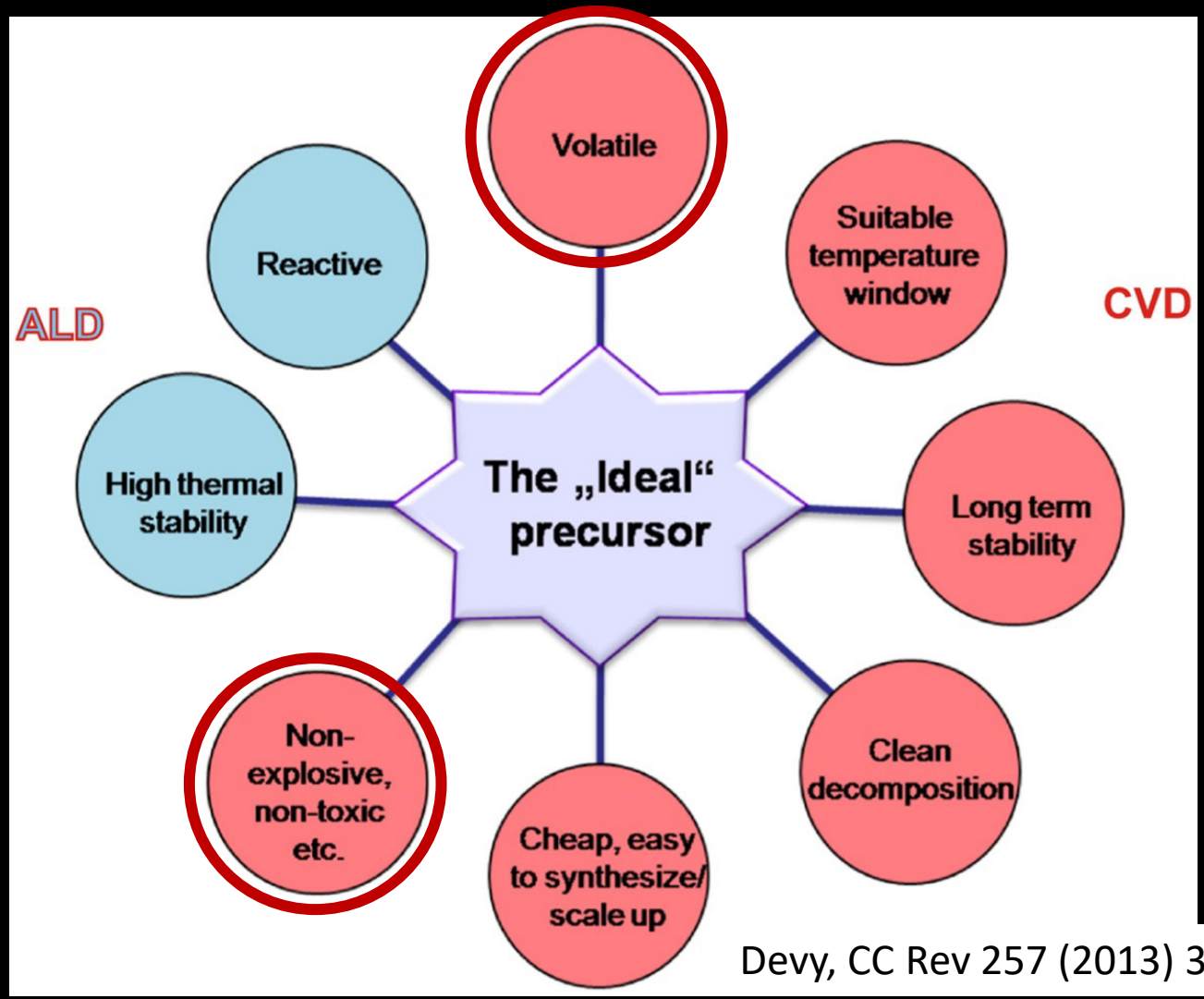
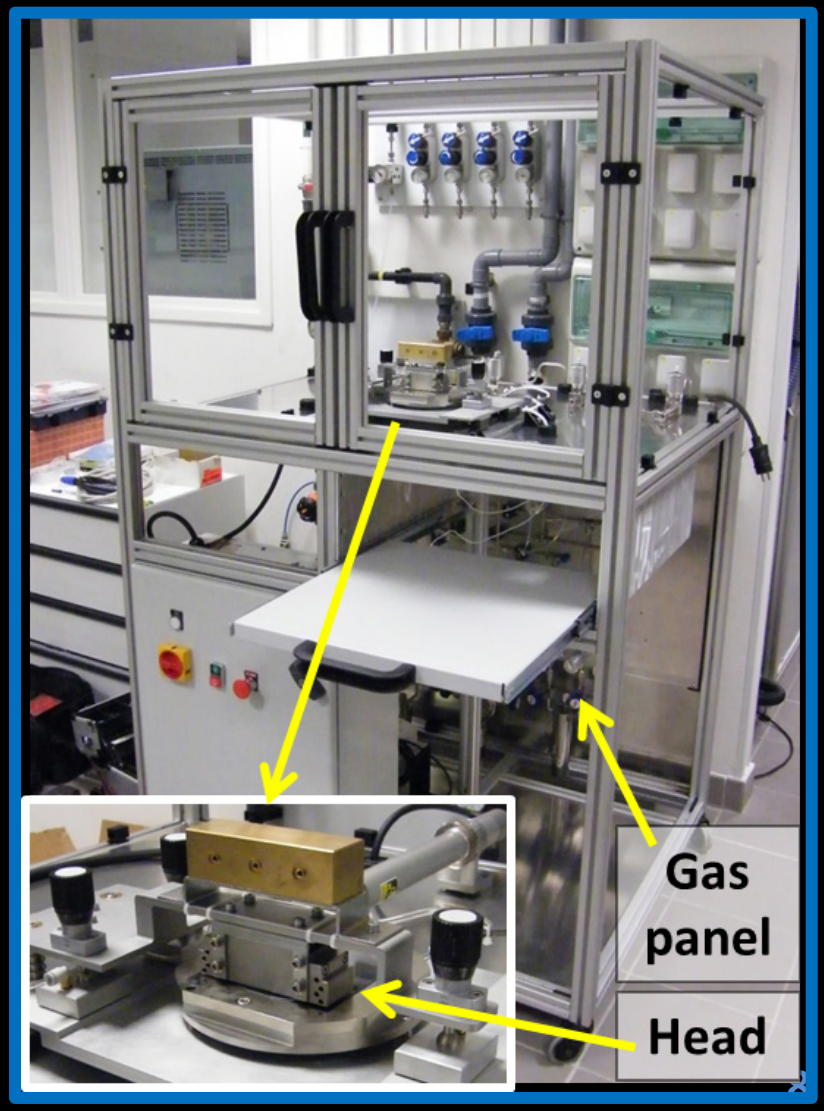


Devy, CC Rev 257 (2013) 3332

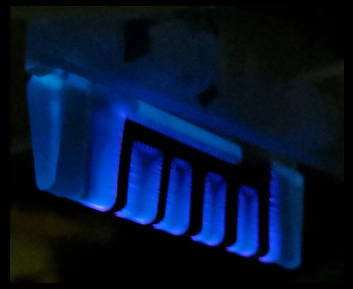


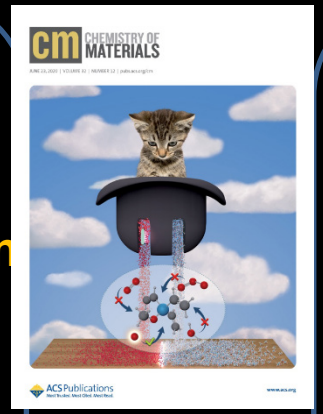
SALD Research at LMGP

SPECIFICATION OF THE SALD	
Deposition Temperature	RT to 350 °C
Deposition Area	1 to 25 cm^2
Growth rate	Up to 2 nm/s
Subtrates	Metal, glass, plastic, tissue,
Maximum Achievable Thickness	Up to several µm

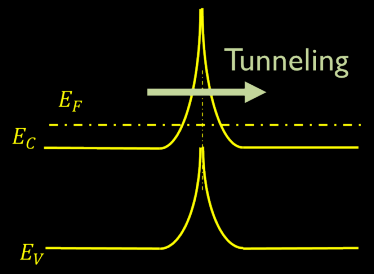
Materials available or in study:
ZnO, Al_2O_3, Al:ZnO, Cu, Cu_2O, CuO, TiO_2, SiO_x, MgO, SnO_2, Ga_2O_3, HfO_2, Ag, CeO_2, ZrO_2, Pd, Hybrids (Metalcones, MOFs, …)

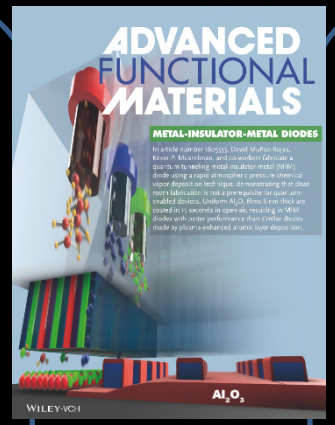
Design & Optimization
- **Atm. Plasma activation**
- **up-scaling/simulation**



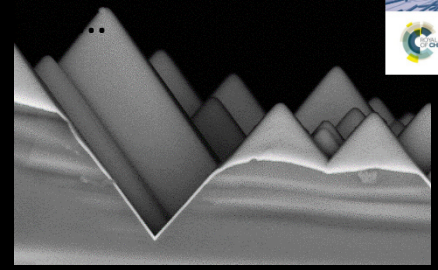


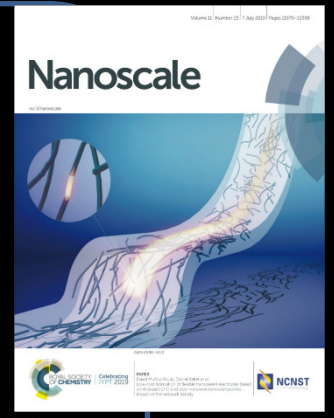
Fundamental studies
- **Effect of open-air processing**
- **New materials**





Applications
- **TCM**
- **PV**
- **Sensors**
- **Res.Switc.**

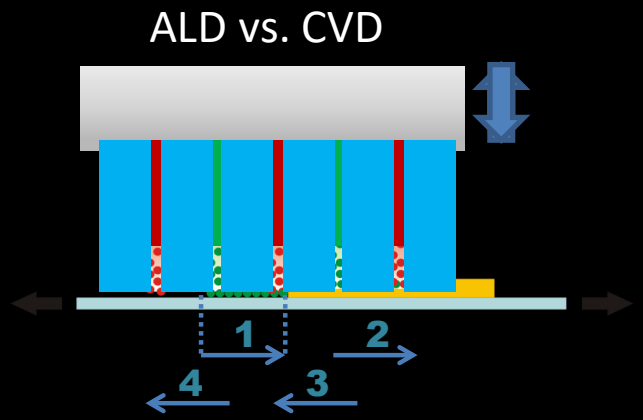


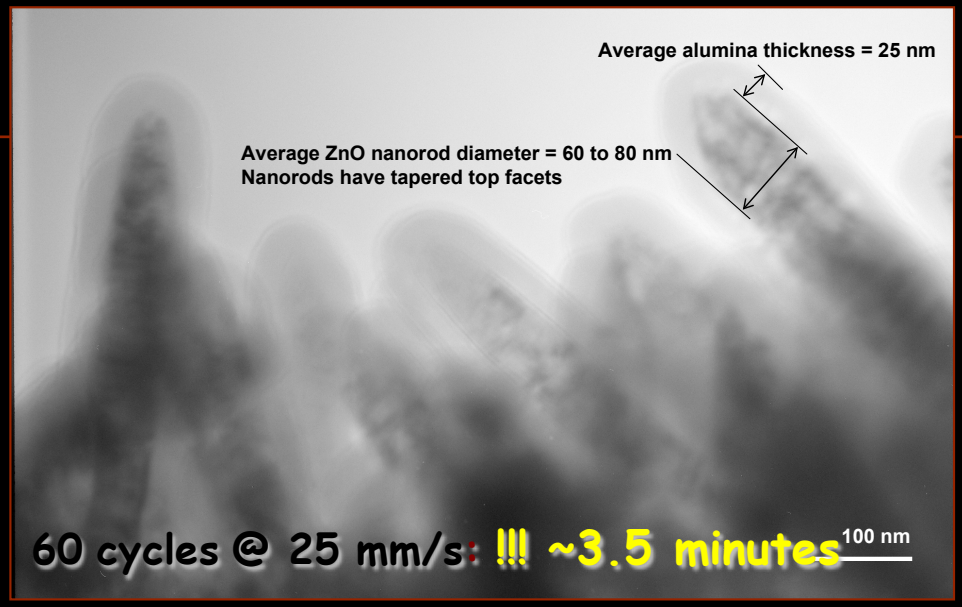


Open-air SALD @ LMGP

20 cycles @ 2 mm/s: ~12 minutes

Possibility to perform CVD





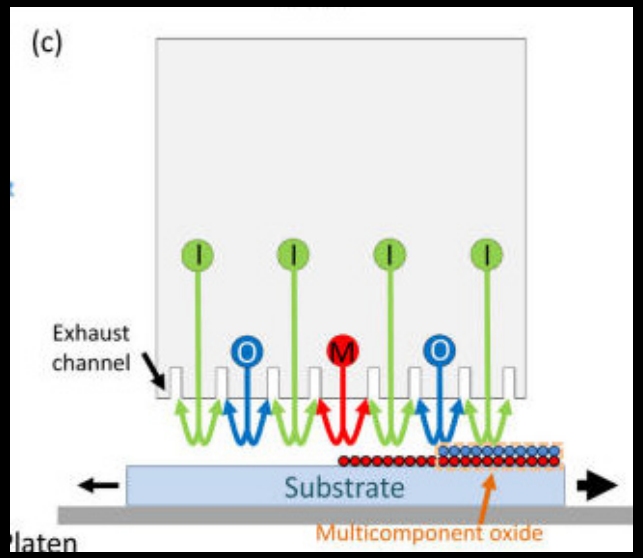
40 cycles @ 2 mm/s: ~25 minutes

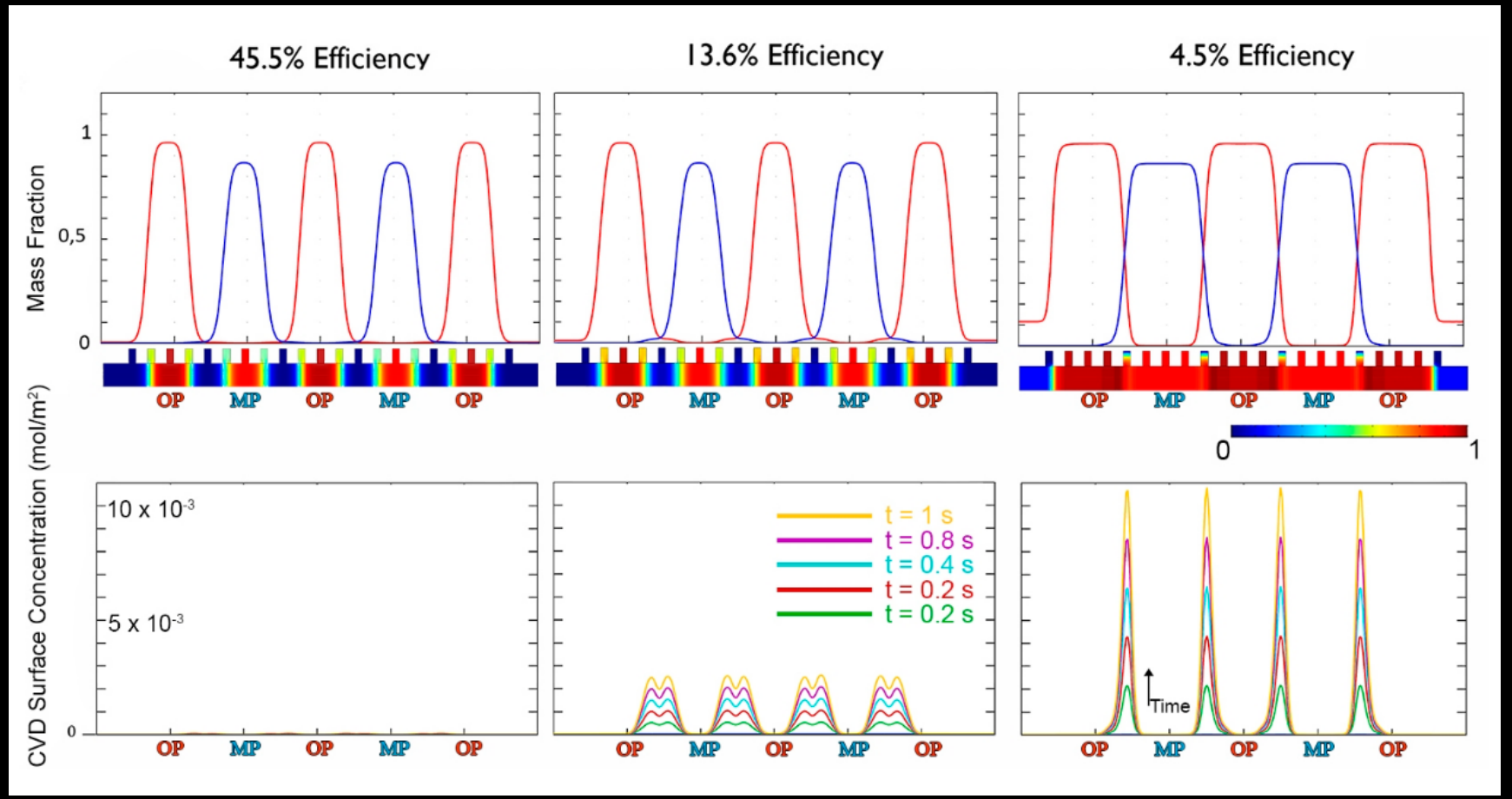
K. Musselman et al. *Nanoscale Horizons*, 2017, 2, 110

Area-selective Deposition

César Masse

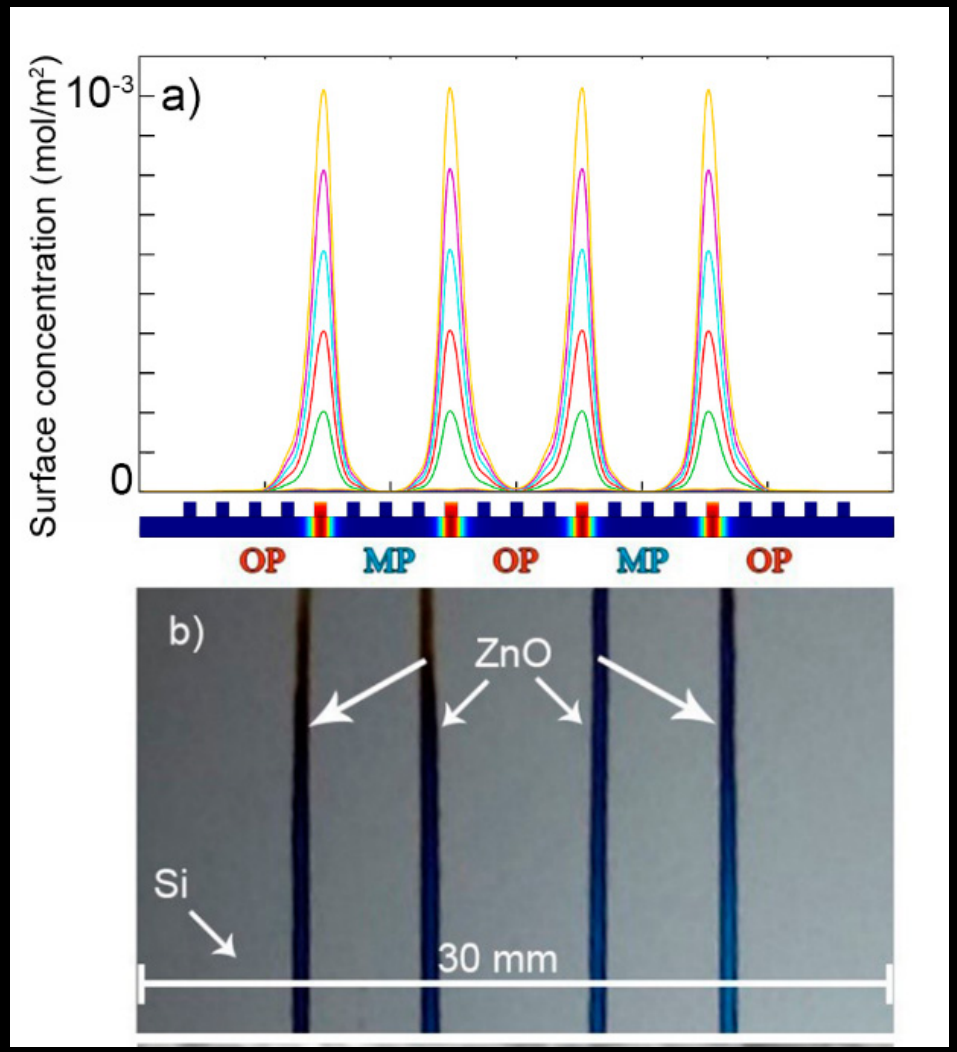
- **CFD simulations:**



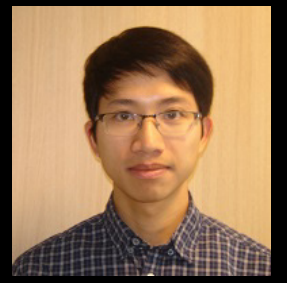


Masse de la Huerta, et al., Coatings, 2018

Different customized SALD heads



Static Deposition SCVD: an alternative approach to selective depostion



Viet Nguyen

César Masse

Masse de la Huerta, et al., Coatings, 2018

Custom heads by 3D printing

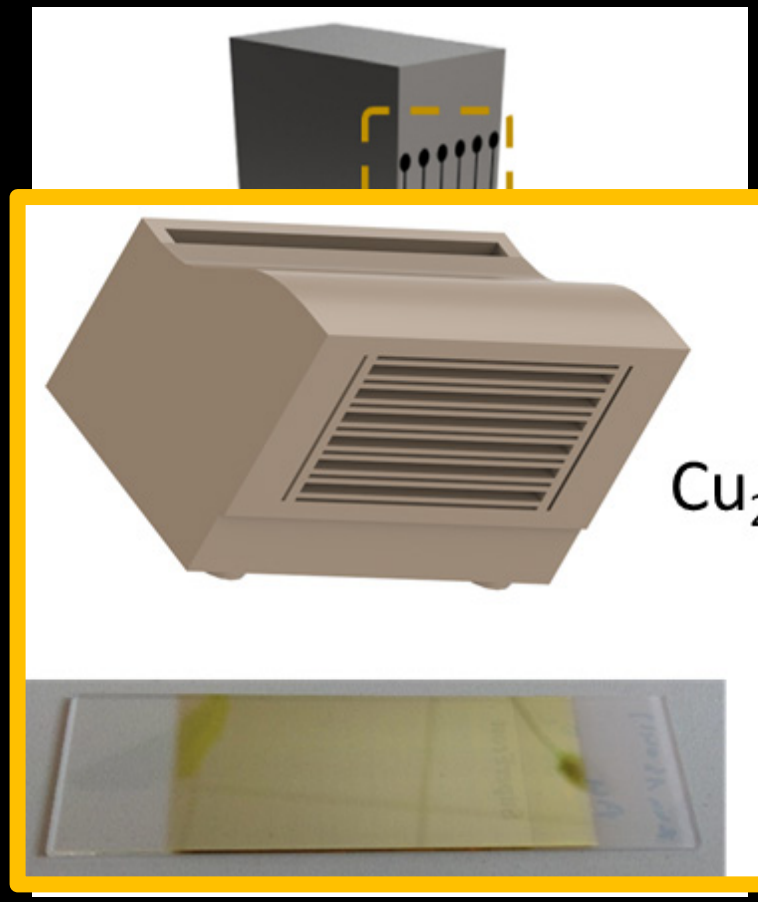
- **3D printing for SALD heads:**

Let’s use 3D printing!

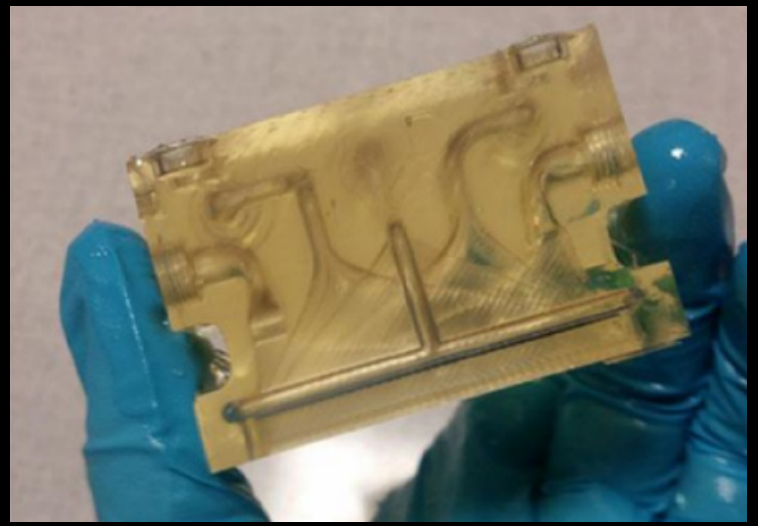
Masse de la Huerta, et al., Adv. Mater. Tech, 2020, 5 (12), 2000657

Custom head by 3D printing

- **3D printing for ASD:**



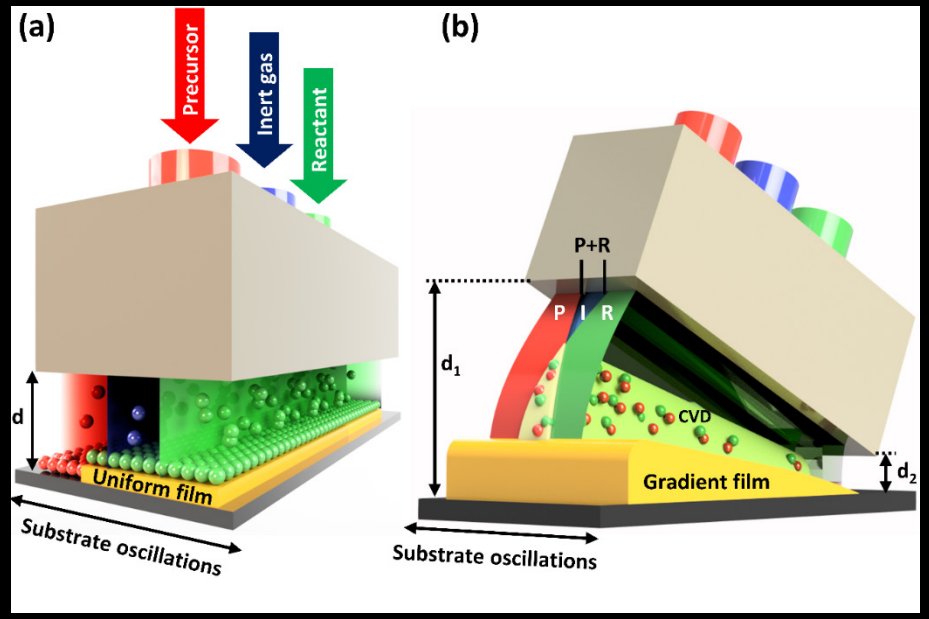
César Masse *Chiara Crivello* *Abdou Sekkat* *Fidel Toldrà*

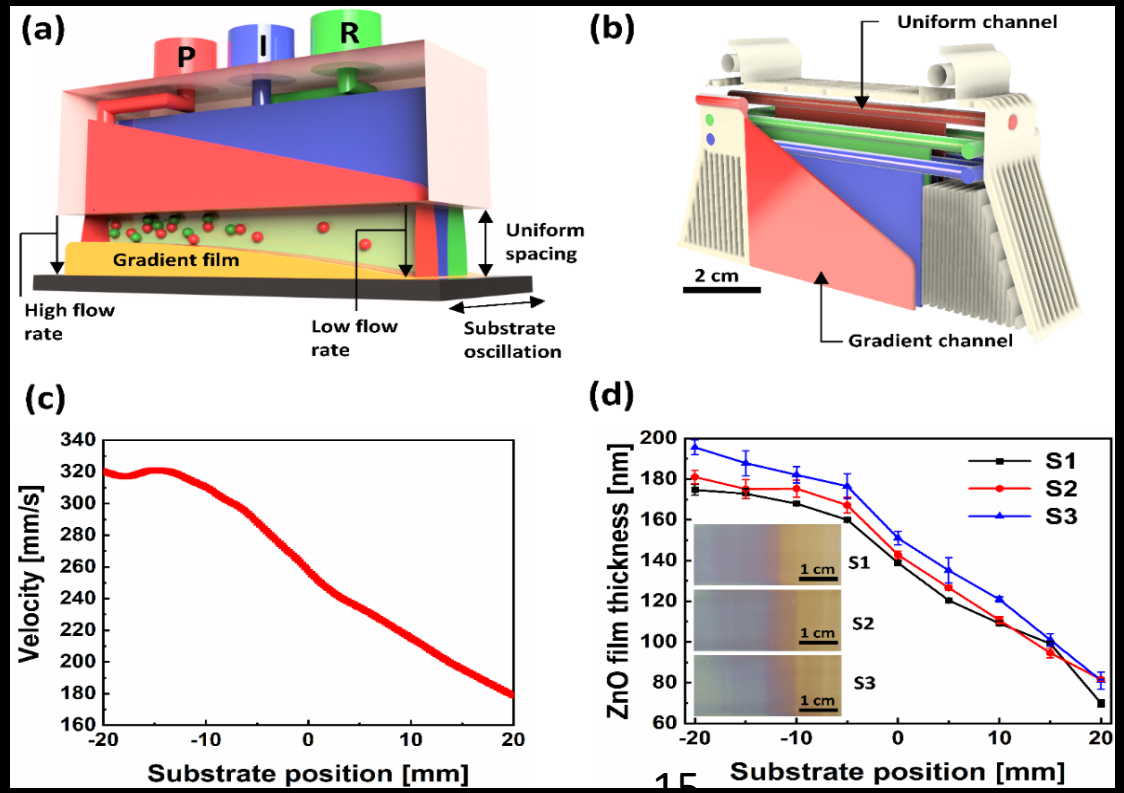


Masse de la Huerta, et al., Adv. Mater. Tech, 2020, 5 (12), 2000657

Combinatorial deposition (Coll. Univ. Waterloo)

- *non-homogeneous samples on purpose: thickness gradient*

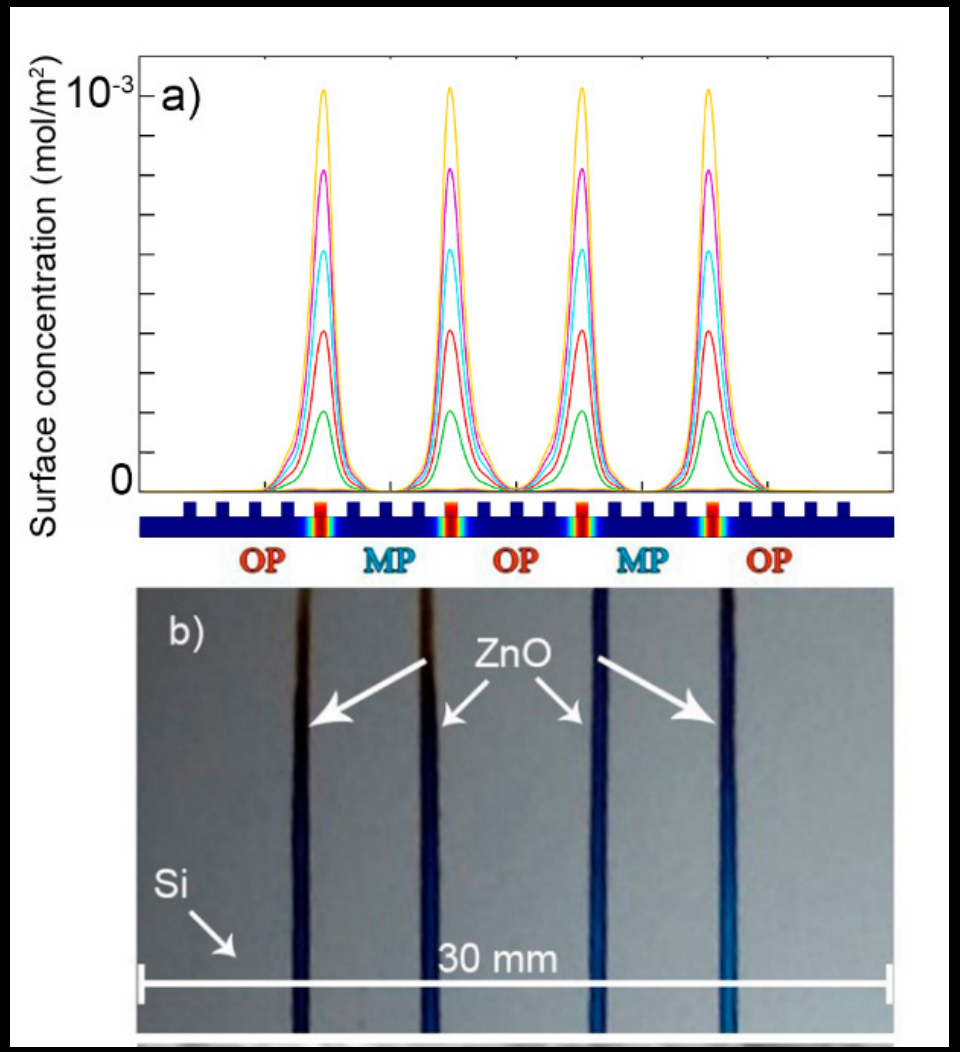




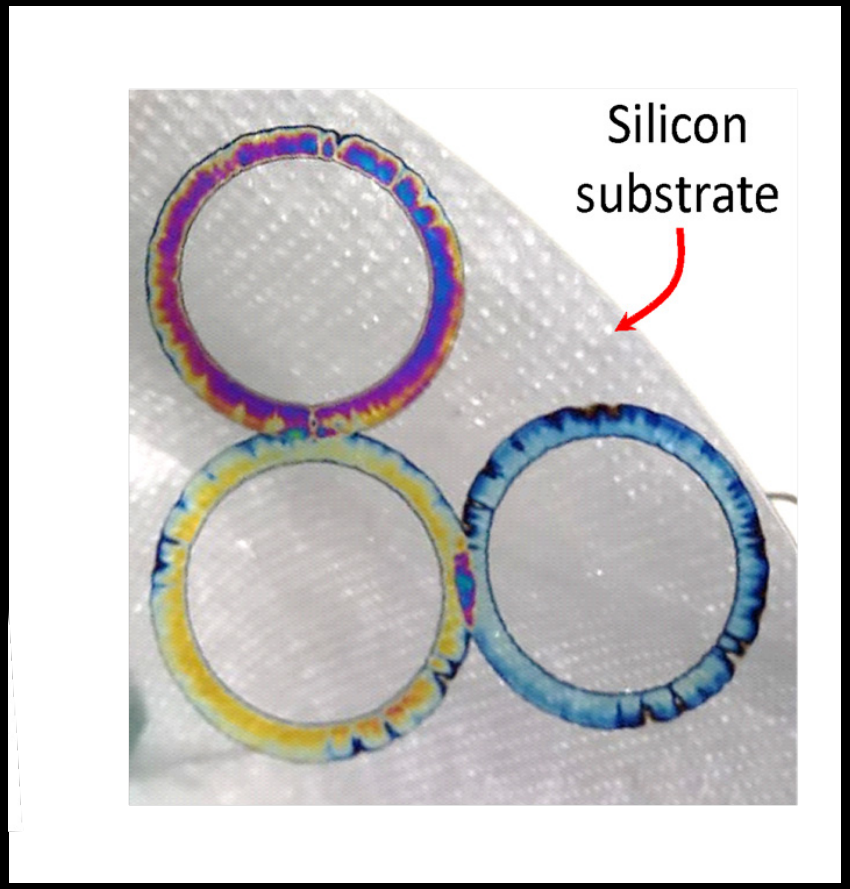
- *3D printed custom heads to be non-homogeneous (simulation)*

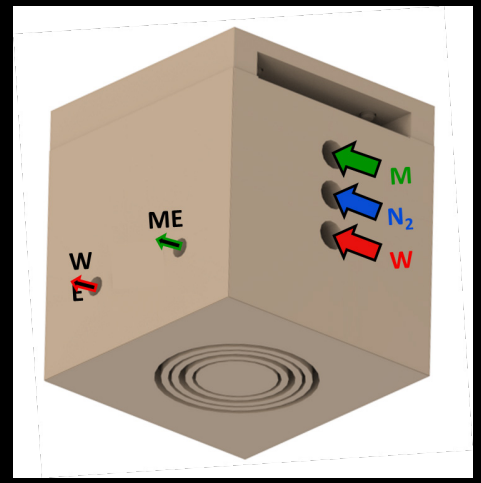
Adv. Funct. Mater. 2021, 31(31), 2103271

Different customized SALD heads



Static Deposition SCVD: an alternative approach to selective depostion

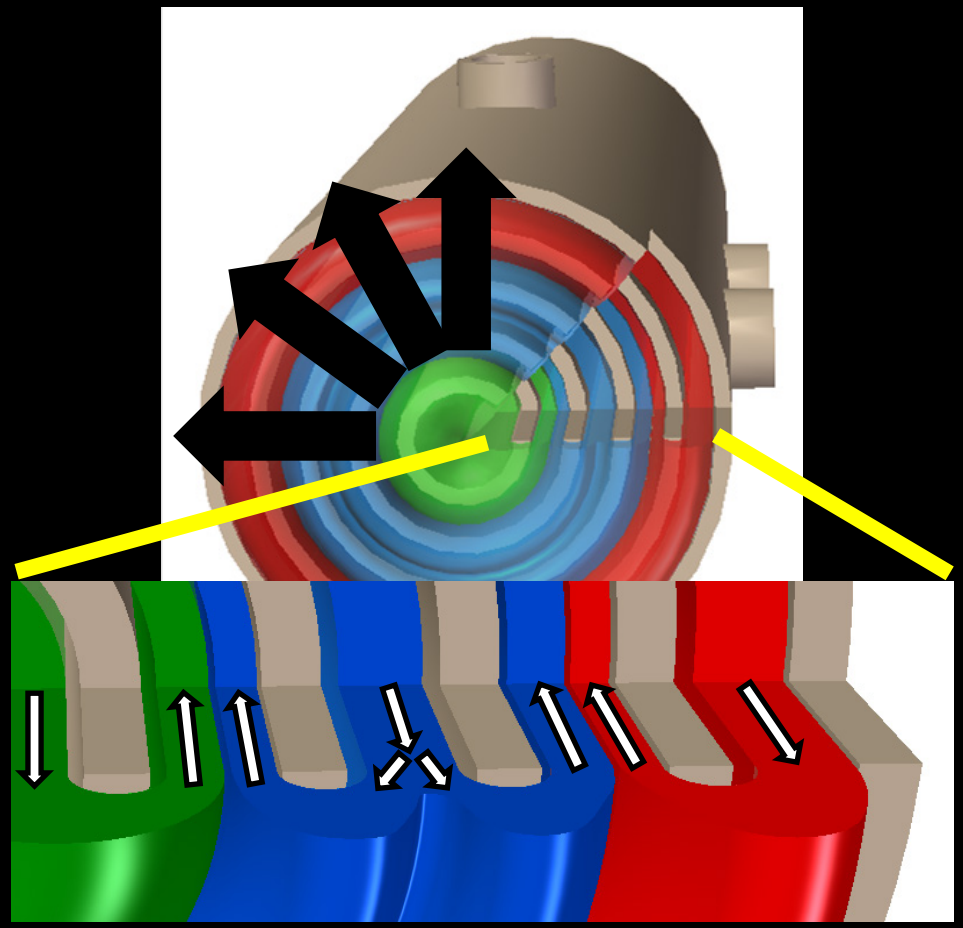


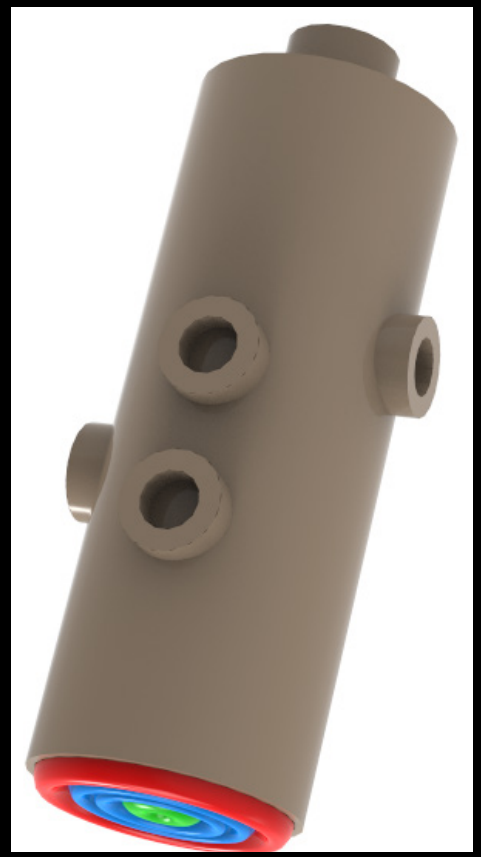


Masse de la Huerta, et al., Adv. Mater. Tech, 2020, 5 (12), 2000657

Scribbling functional materials

SALD PEN: Concentric channels. Possible to move in any direction

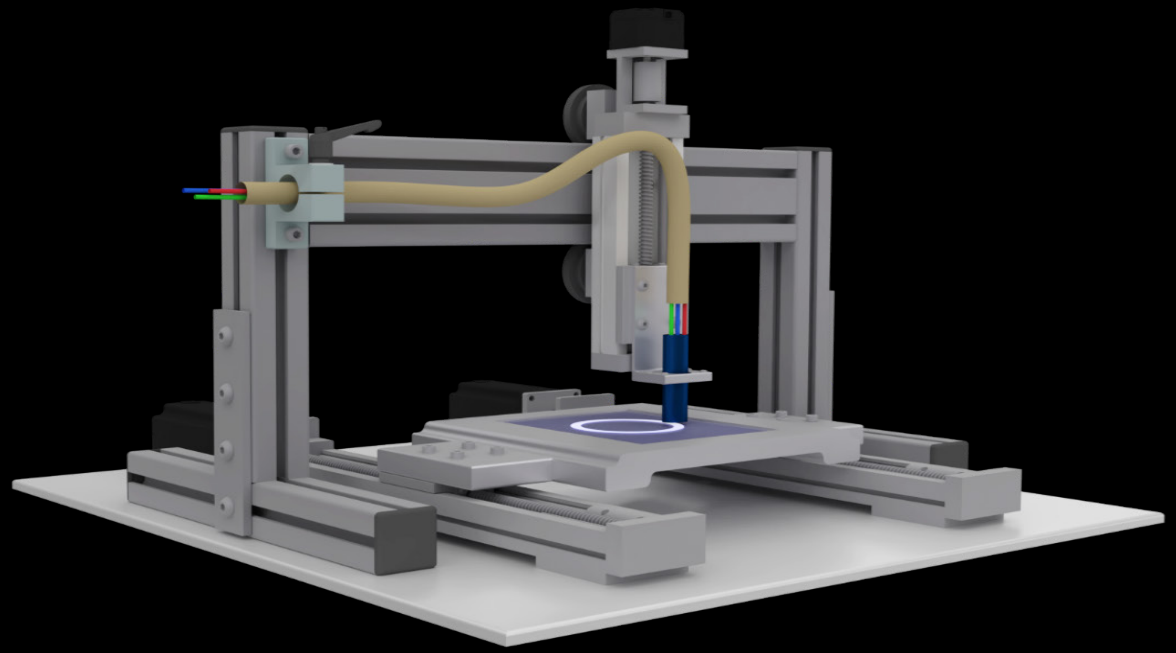




Masse de la Huerta, et al., Adv. Mater. Tech, 2020, 5 (12), 2000657

Scribbling functional materials

- **SALD PEN: Concentric channels. GAS-PHASE 3D printing of functional materials with nanometric resolution in Z**

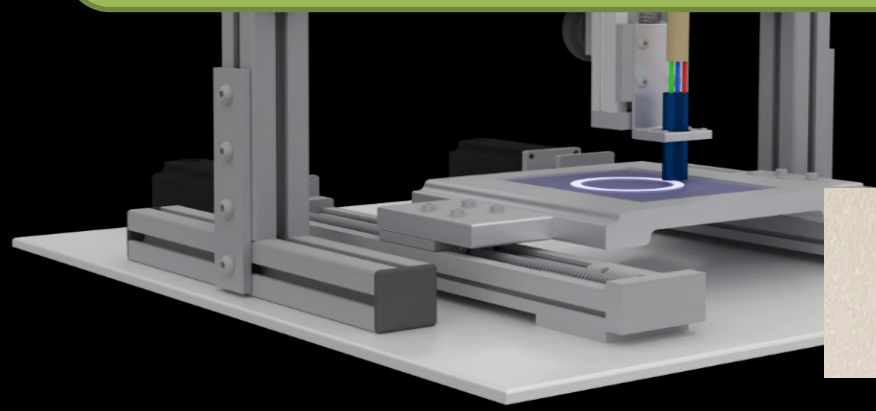


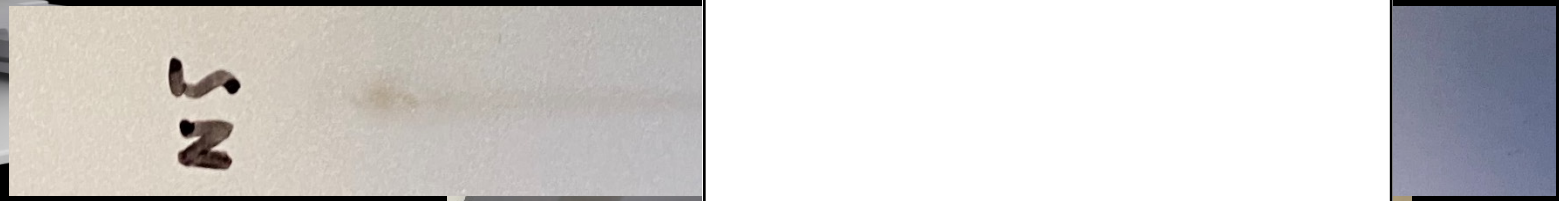
Masse de la Huerta, et al., Adv. Mater. Tech, 2020, 5 (12), 2000657

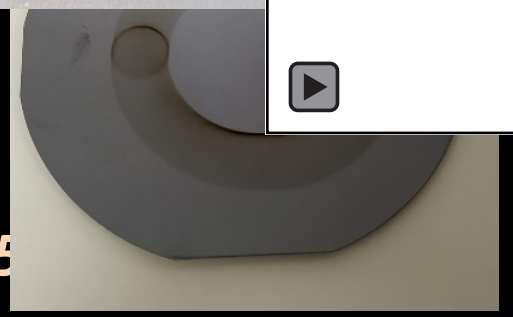
Scribbling functional materials

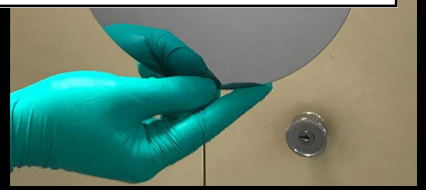
- **SALD PEN: Concentric channels. GAS-PHASE 3D printing of functional materials with nanometric resolution in Z**

New gas-phase 3D printing approach with nanometric resolution in Z









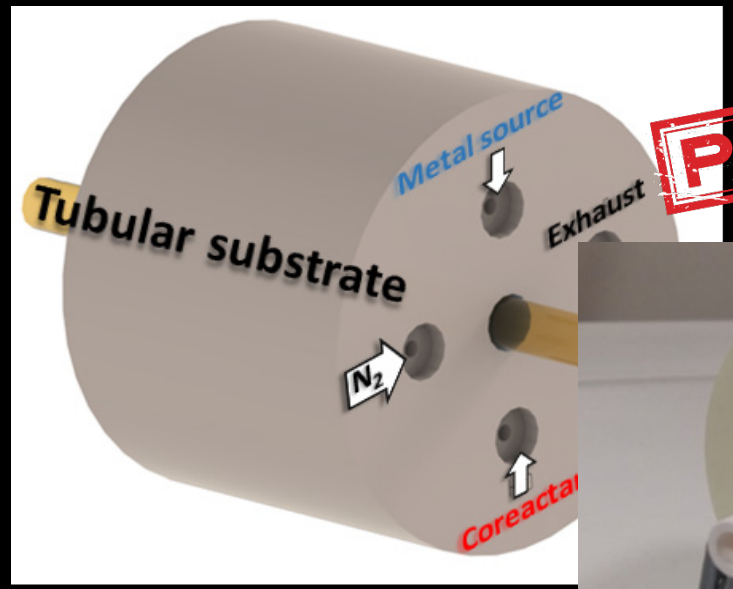
Masse de la Huerta, et al., Adv. Mater. Tech, 2020, 5

SALD on non-flat substrates?

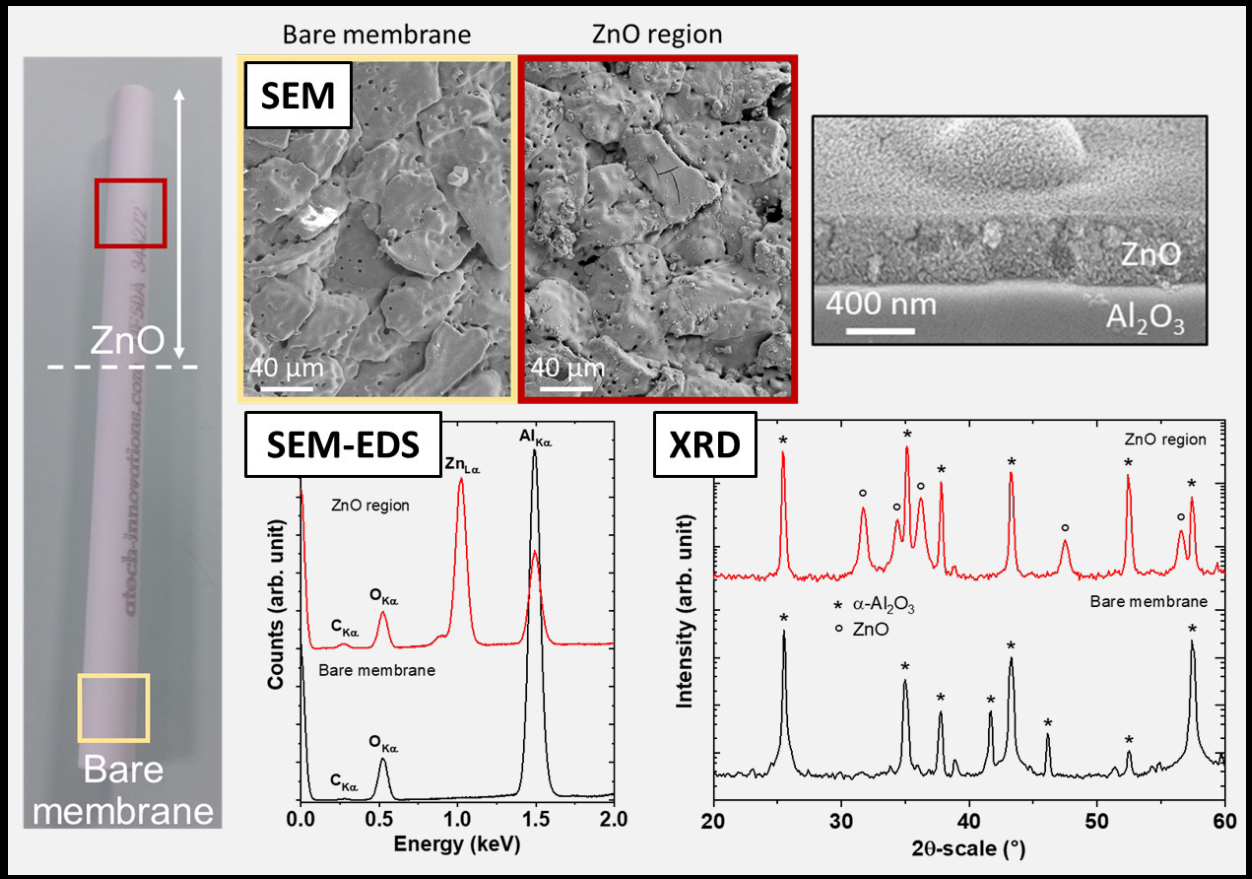
Clement Lausecker

Fidel Toldrà

- **Custom SALD close proximity head for tubular-cylindric substrates**



PATENTED



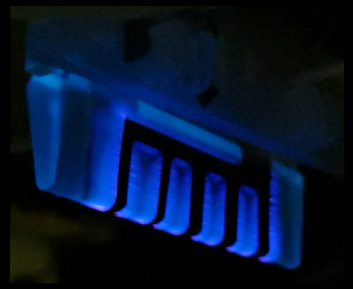
F. Toldra-Reig et al., submitted. Patent Pending

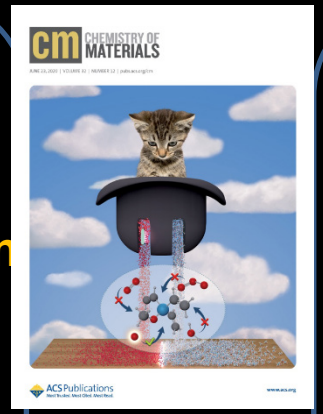
SALD Research at LMGP

SPECIFICATION OF THE SALD	
Deposition Temperature	RT to 350 °C
Deposition Area	1 to 25 cm^2
Growth rate	Up to 2 nm/Cycle
Subtrates	Metal, glass, plastic, tissue,
Maximum Achievable Thickness	Up to several µm

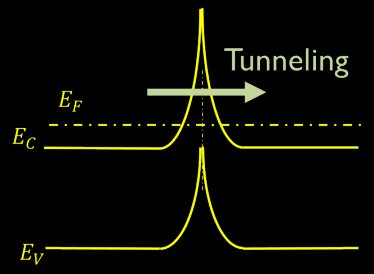
Materials available or in study:
ZnO, Al_2O_3, Al:ZnO, Cu, Cu_2O, CuO, TiO_2, SiO_x, MgO, SnO_2, Ga_2O_3, HfO_2, Ag, CeO_2, ZrO_2, Hybrids (Metalcones, MOFs, …)

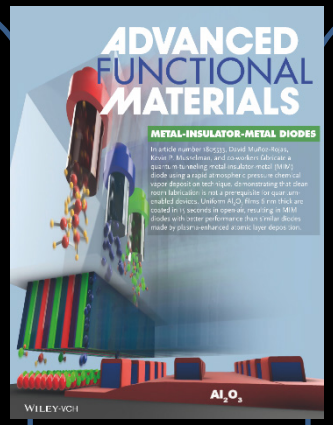
Design & Optimization
- Atm. Plasma activation
- up-scaling/simulation



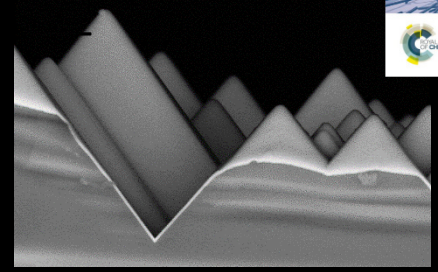


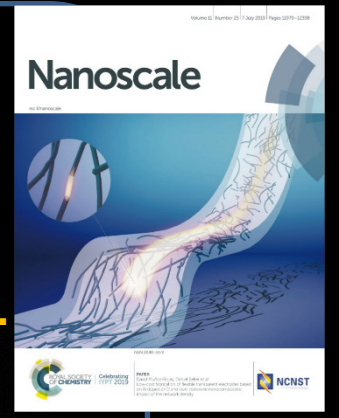
Fundamental studies
- Effect of open-air processing
- New materials



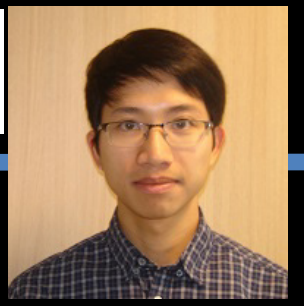


Applications
- TCM
- PV
- Sensors
- Res.Switc.





Effect of Open-air processing



Viet Nguyen

Deposition of Al:ZnO, as Transparent Conductive Oxide (TCO)

Technique	T °C	t (nm)	μ ($cm^2 V^{-1} s^{-1}$)	N (cm^{-3})	ρ (Ω cm)
PLD					-5
DC Spu					4
RF Spu					4
MOCV					-4
ALD					-3
SALD-TNO	200	320	5	$5,0x10^{20}$	$2,0x10^{-3}$
SALD-LMGP	200	210	2,6	$4,25x10^{20}$	$5.6x10^{-3}$

New theoretical model that takes into account tunneling through the GBs in highly degenerated semiconductors (TCO)

State-of-the-art, comparable to Tin-doped In oxide (ITO), standard TCO

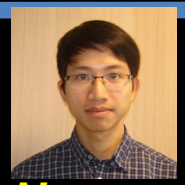
Why such a low mobility??

J. Y. W. Seto, J. App. Phys. 46 (1975) 5247. >3000 citations!

V. H. Nguyen et al. Mat. Horizons, 2018

Atmospheric-Plasma-Activated SALD

ANR project DESPATCH, coll GREMI, LTM: Plasma deposition of SiO_2

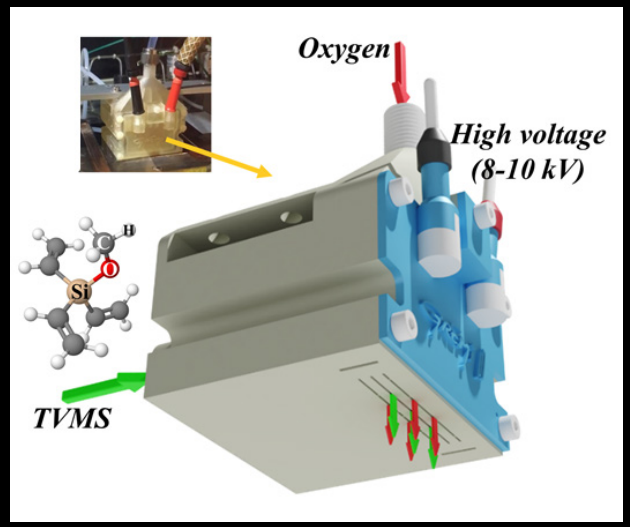


Viet Nguyen

Direct Barrier Discharge (DBD)

Atmospheric

Integration in SALD head



SiO_2 on Si from RT to 150 °C

V. Nguyen, Chem. Mater, 2020, 32, 5153.

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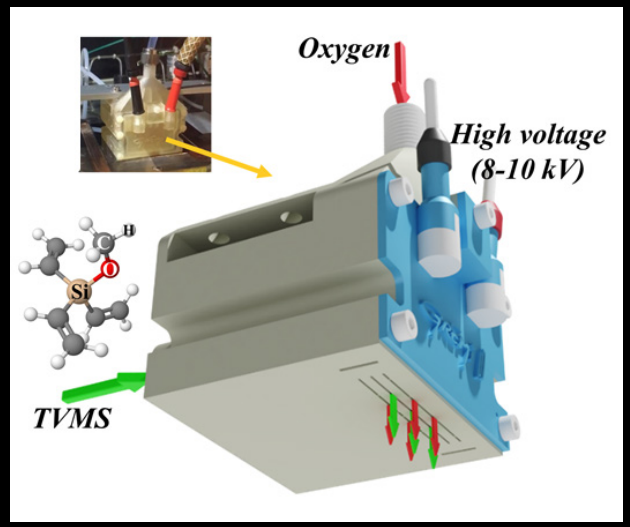
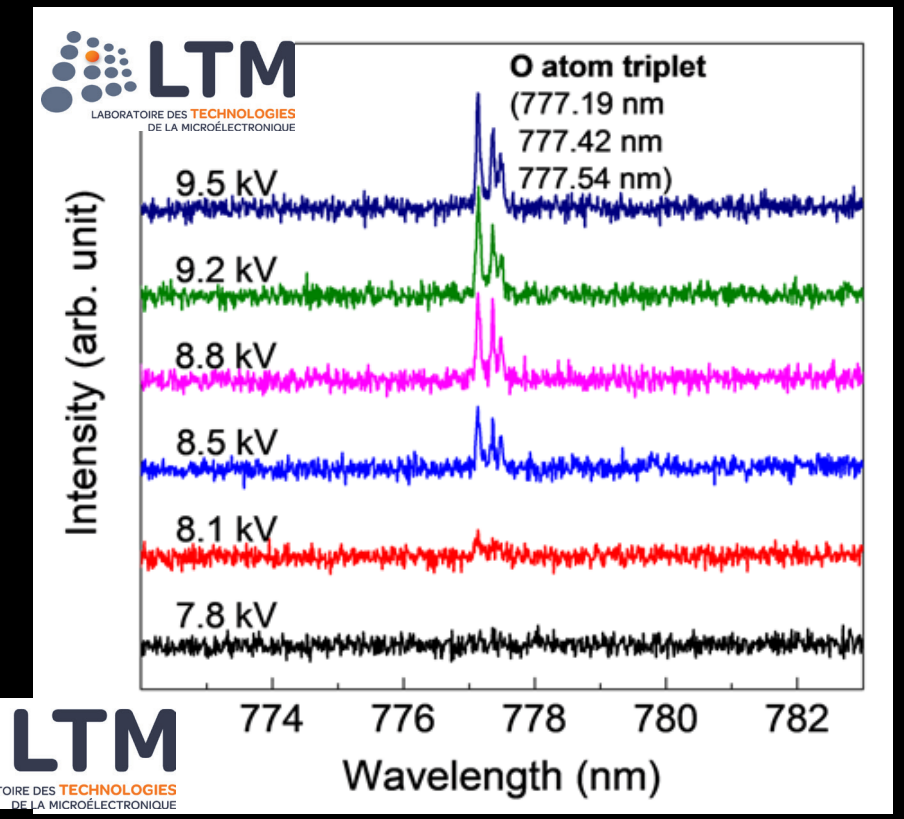


Optical Emission Spectroscopy



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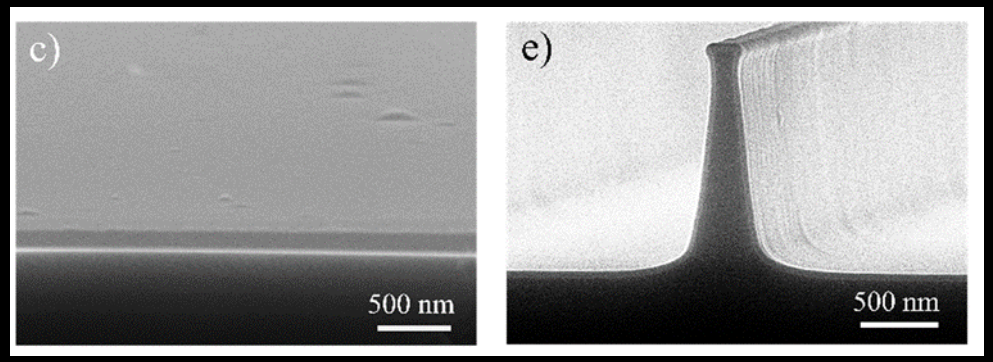
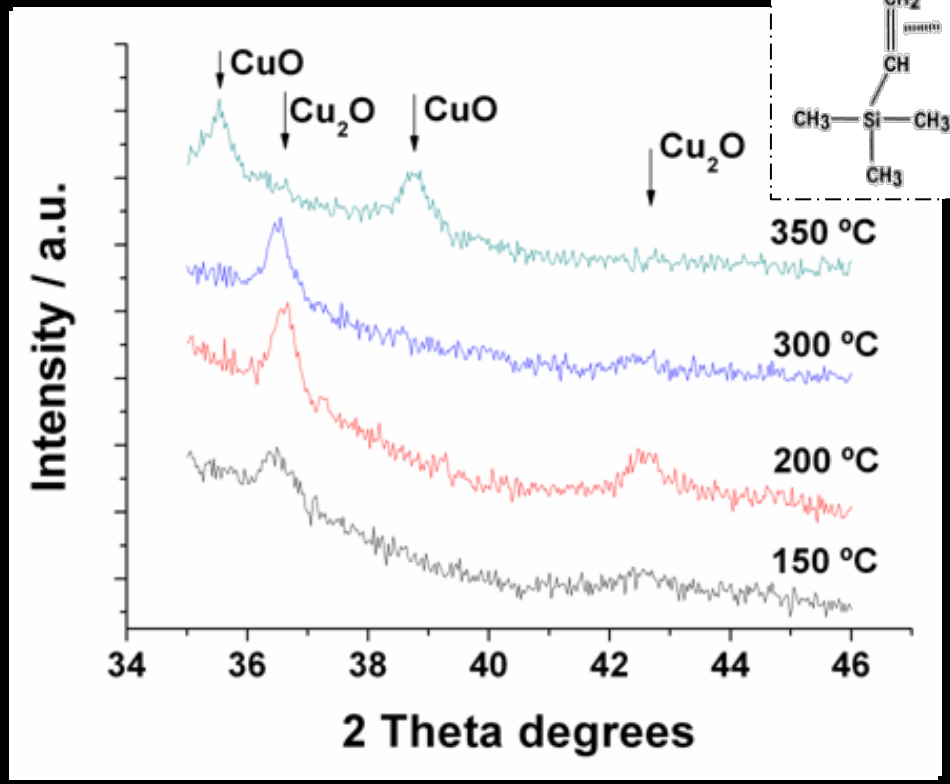


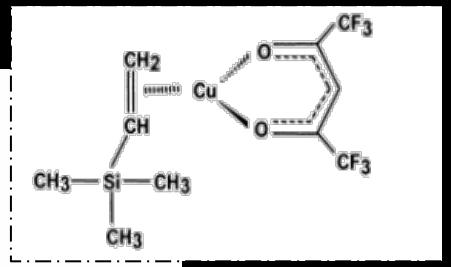
V. Nguyen, Chem. Mater, 2020, 32, 5153.

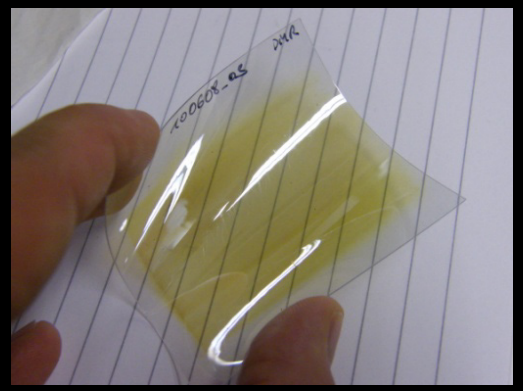
First SALD deposition of Cu_2O back in 2012

Cu_2O: abundant elem. Many applications

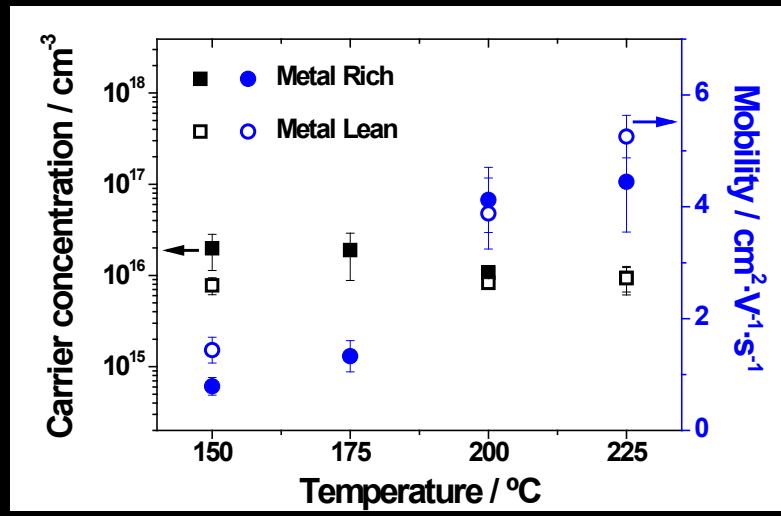
Cupraselect (Cu(tmvs)(hfac), Cu^+) + H_2O Prec. heated at 65 °C

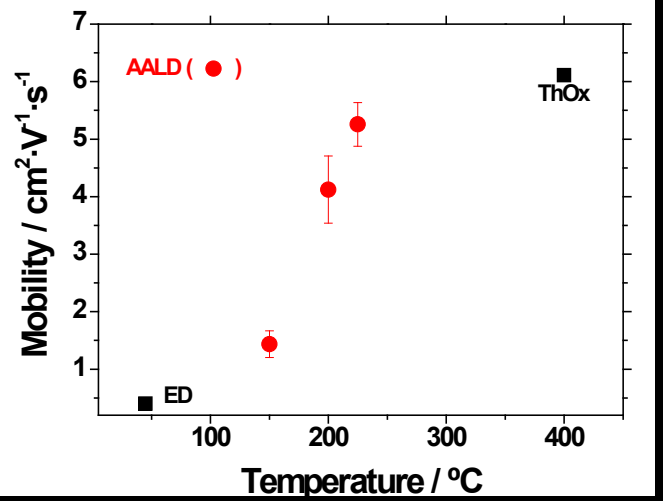






Very good transport prop. NO CLUE WHY. Non-stable precursor!!





D. Muñoz-Rojas et al, AIP advances , 2012 A. Marin et al. Adv. Func. Mater.., **2013**

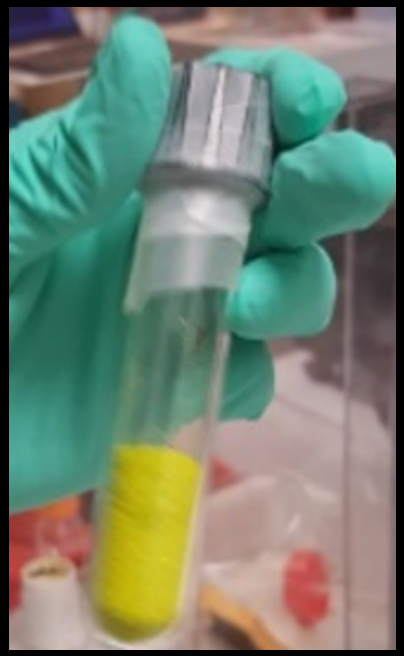
Cu_2O from a "new" solid precursor

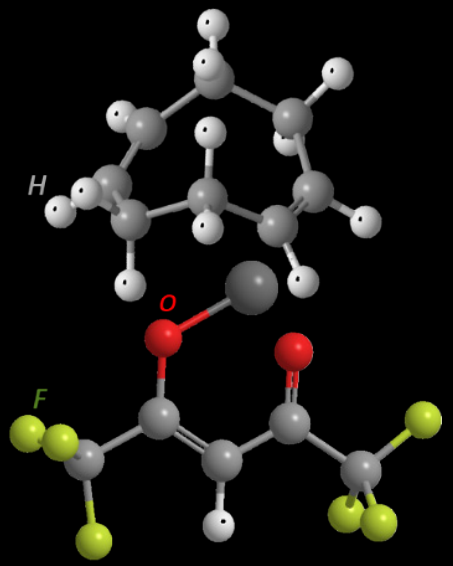
Eco-SESA
Université Grenoble Alpes

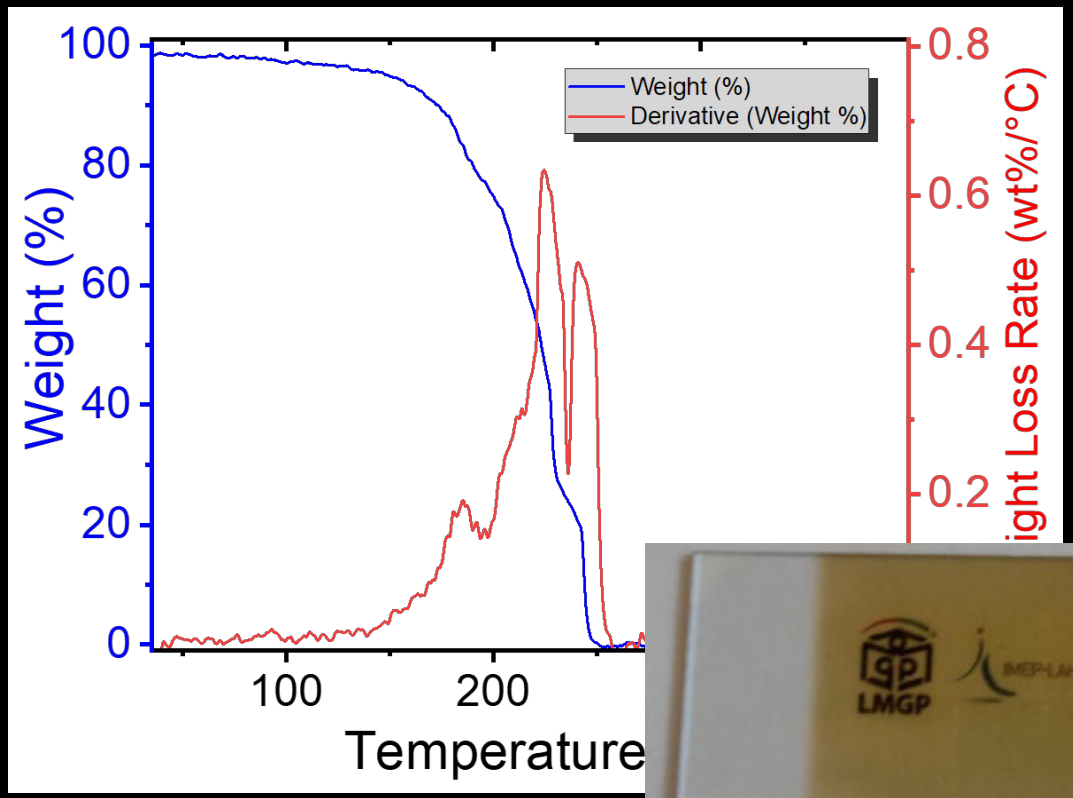
Abdou Sekkat

IDEX CDP project Eco-SESA: Cu_2O for all-oxide solar cells/harvesters

Cu_2O, abundant & non-toxic, many applications: transparent electronics







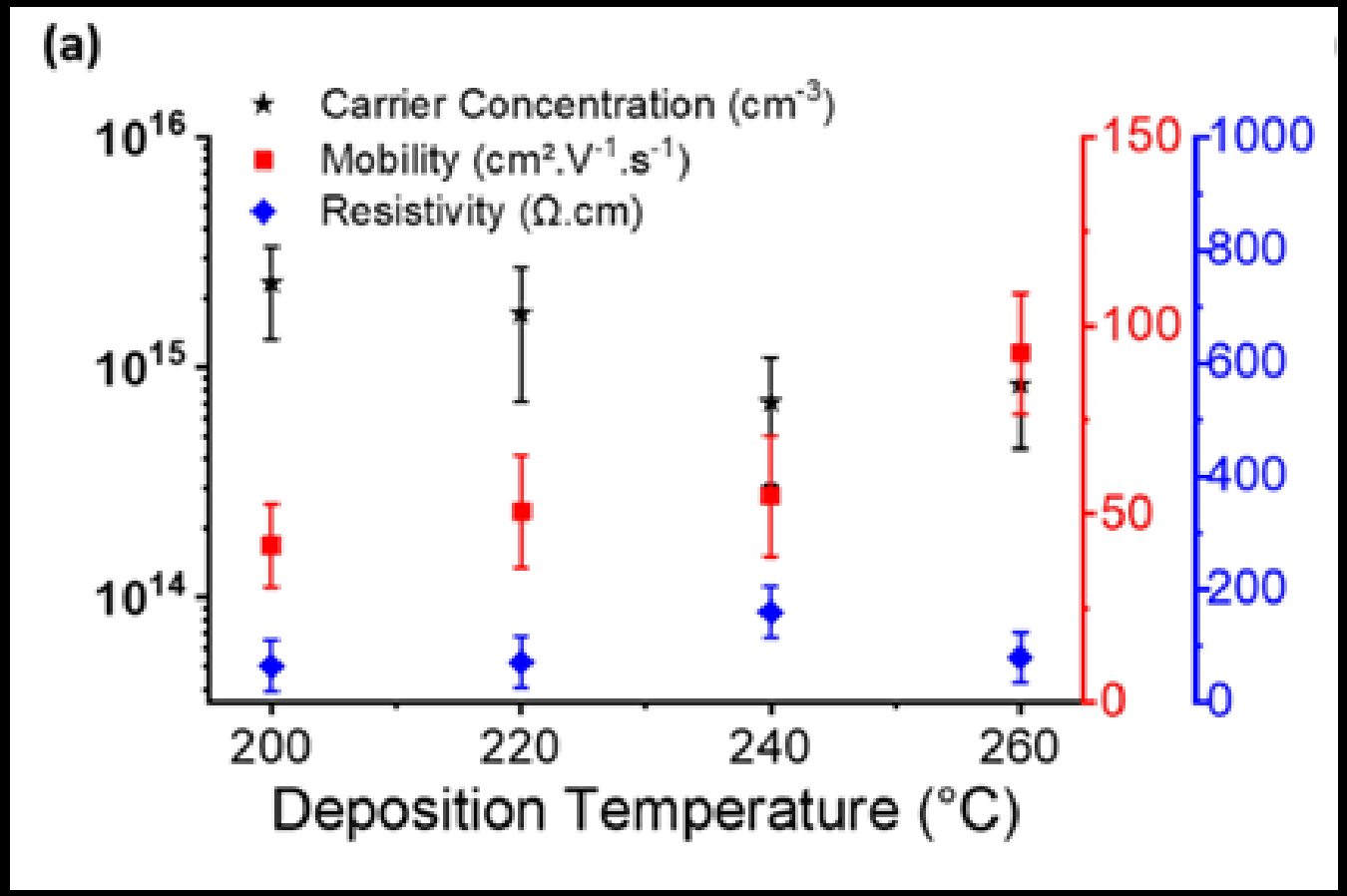
Solid Precursor, never used for CVD, ALD of Cu_2O: Cu(cod)(hfac), Cu^+

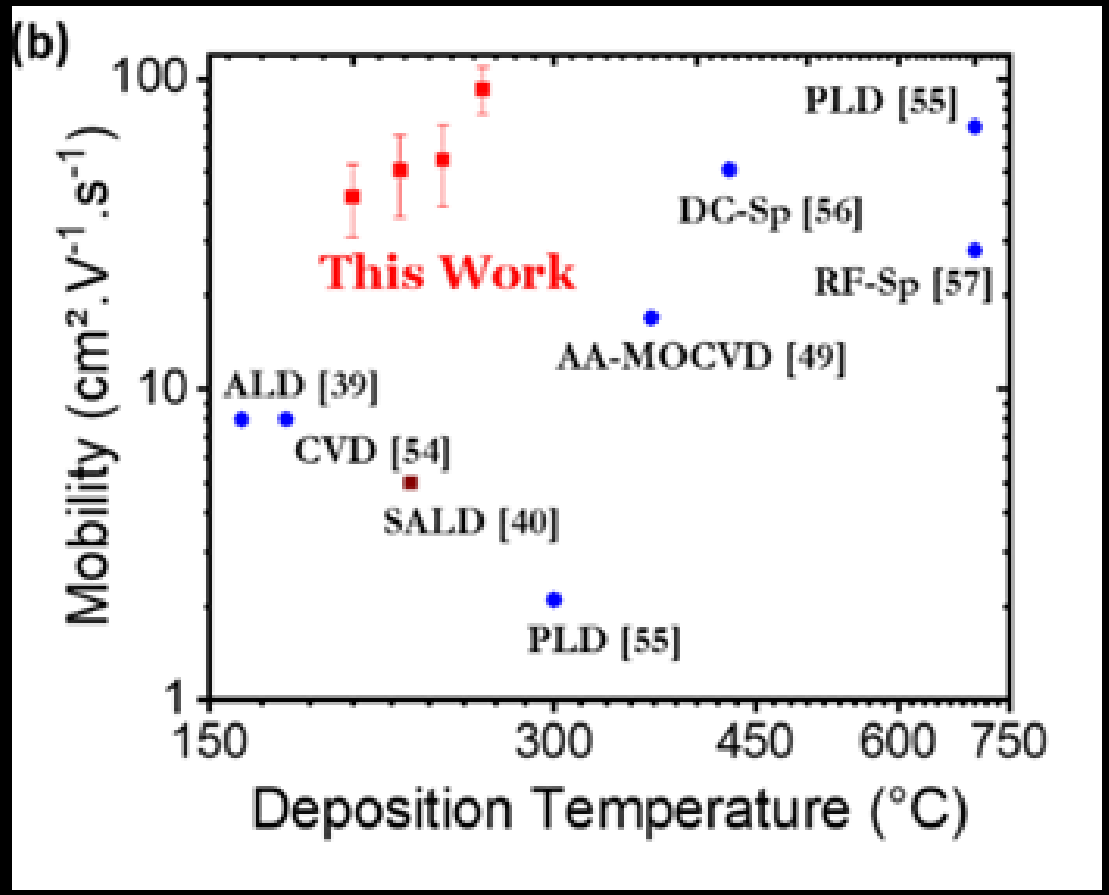
A. Sekkat, Nature ComMat 2021

Cu_2O from a "new" solid precursor

Transport properties

Record mobility values! Close to SC Cu_2O. 10 times less charge concentration than with Cu(tmvs)(hfac)



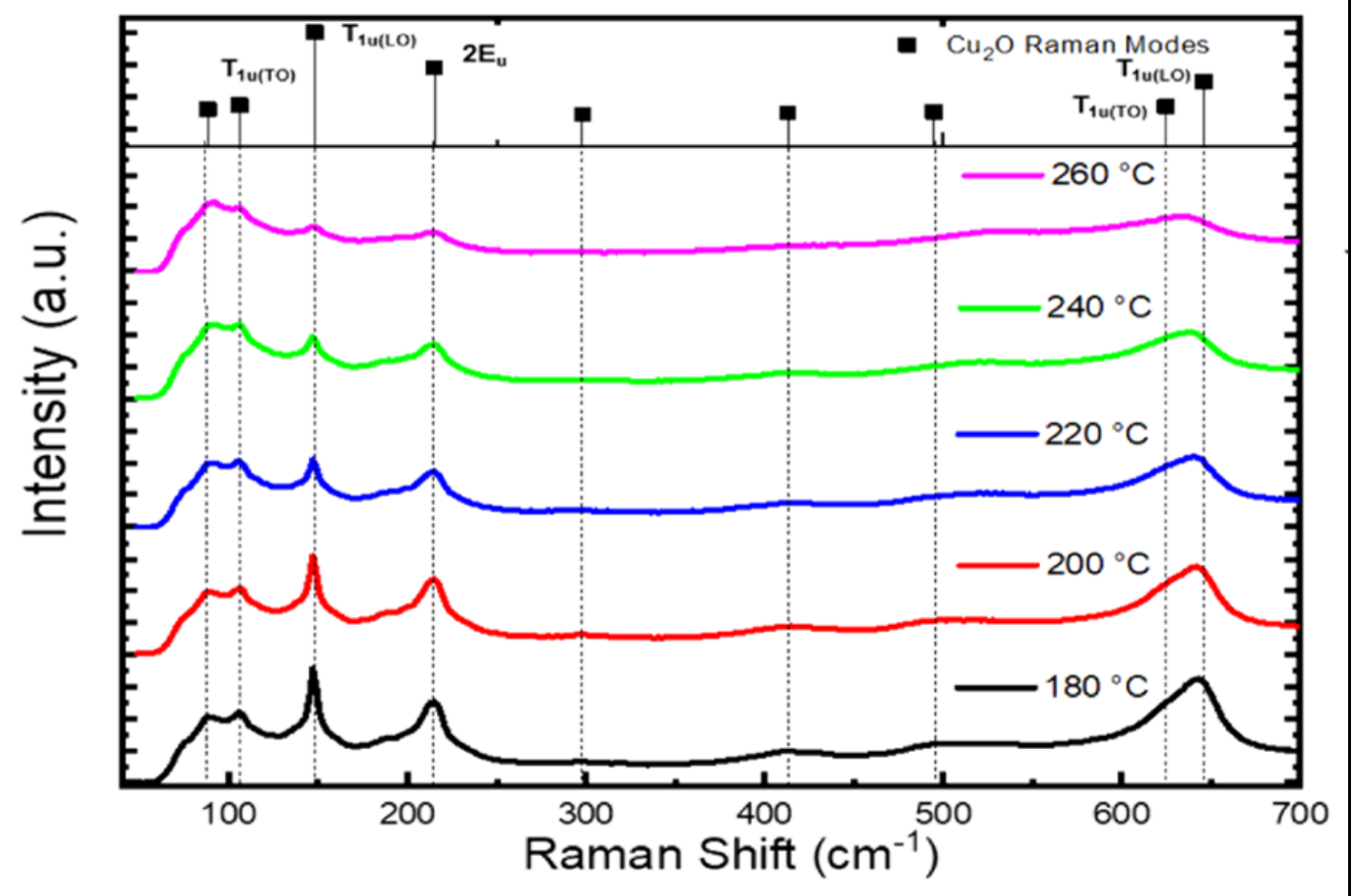


Cu(cod)(hfac) solid precursor

A. Sekkat, Nature ComMat 2021 (Highlighted in Nature Portfolio)

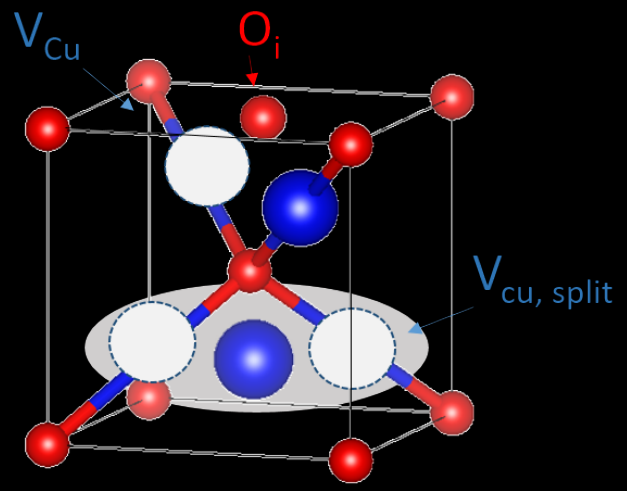
Cu_2O from a "new" solid precursor

Raman comes to the rescue!!



Sander, T et Al (2014).
Physical Review B, 90(4).

The T_{1u} modes measured around 150 and 645 cm^{-1} correspond to phonons not at the zone center: they are activated by defect namely V_{cu}, $V_{cu,split}$ and O_i

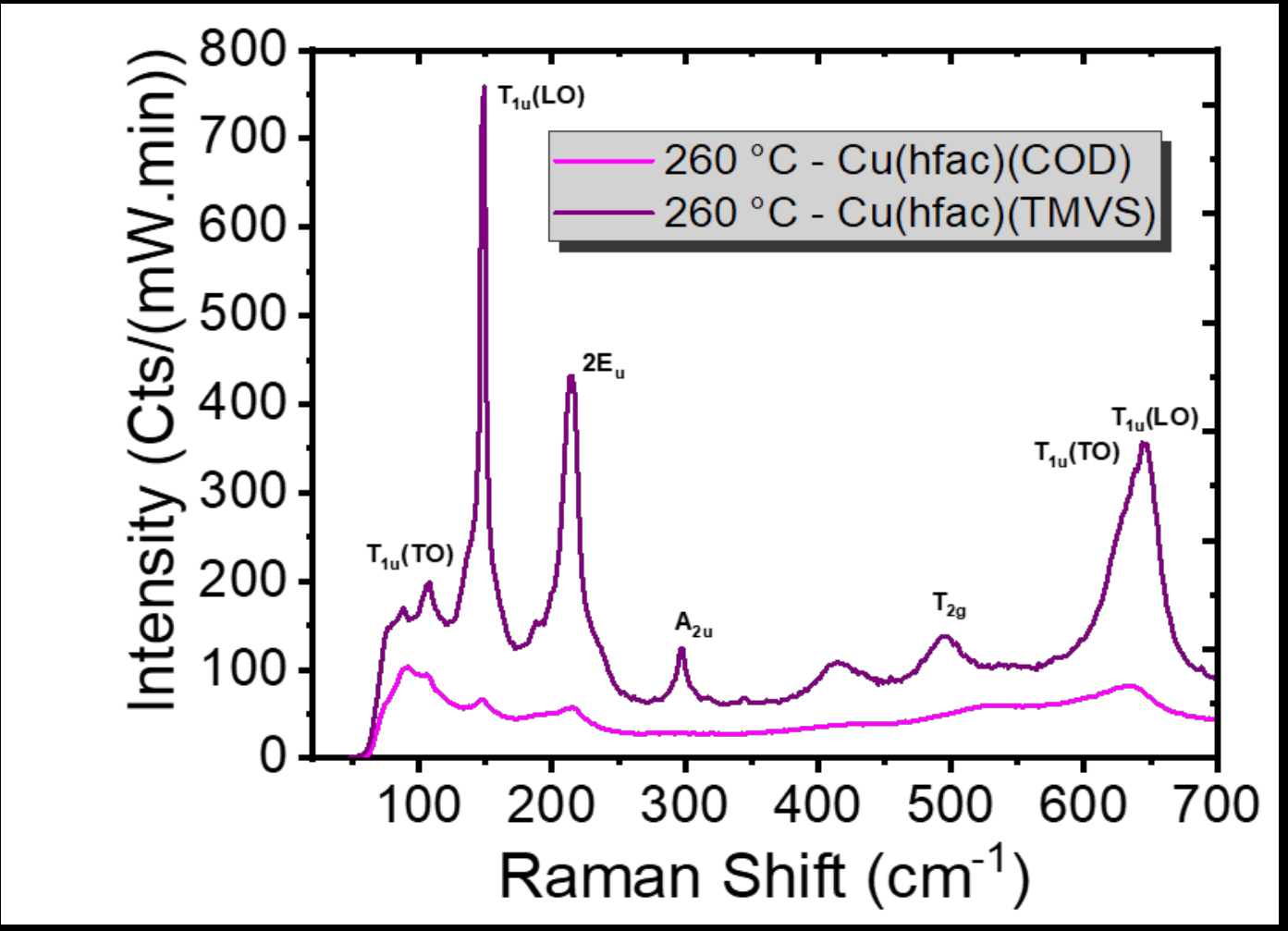


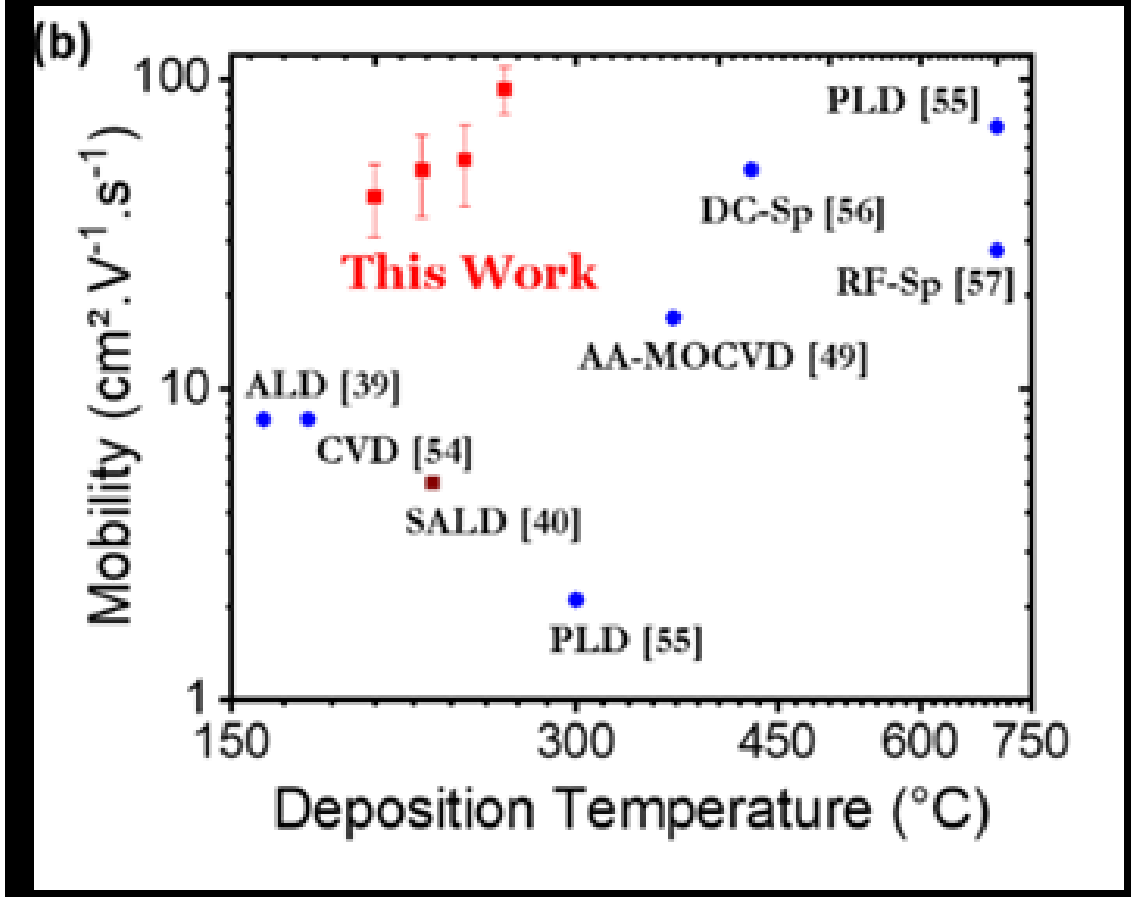
A. Sekkat, Nature ComMat 2021

Cu_2O from a "new" solid precursor

Transport properties

Strong effect of temperature and precursor used on the amount of defects (copper vacancies)

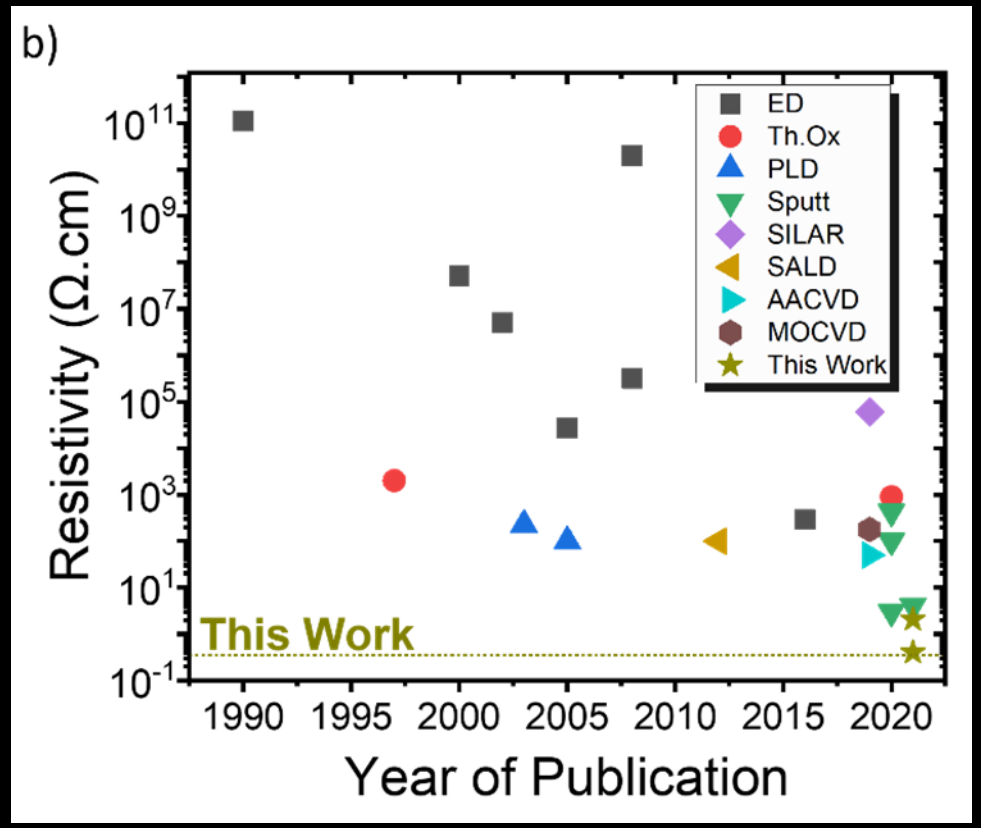


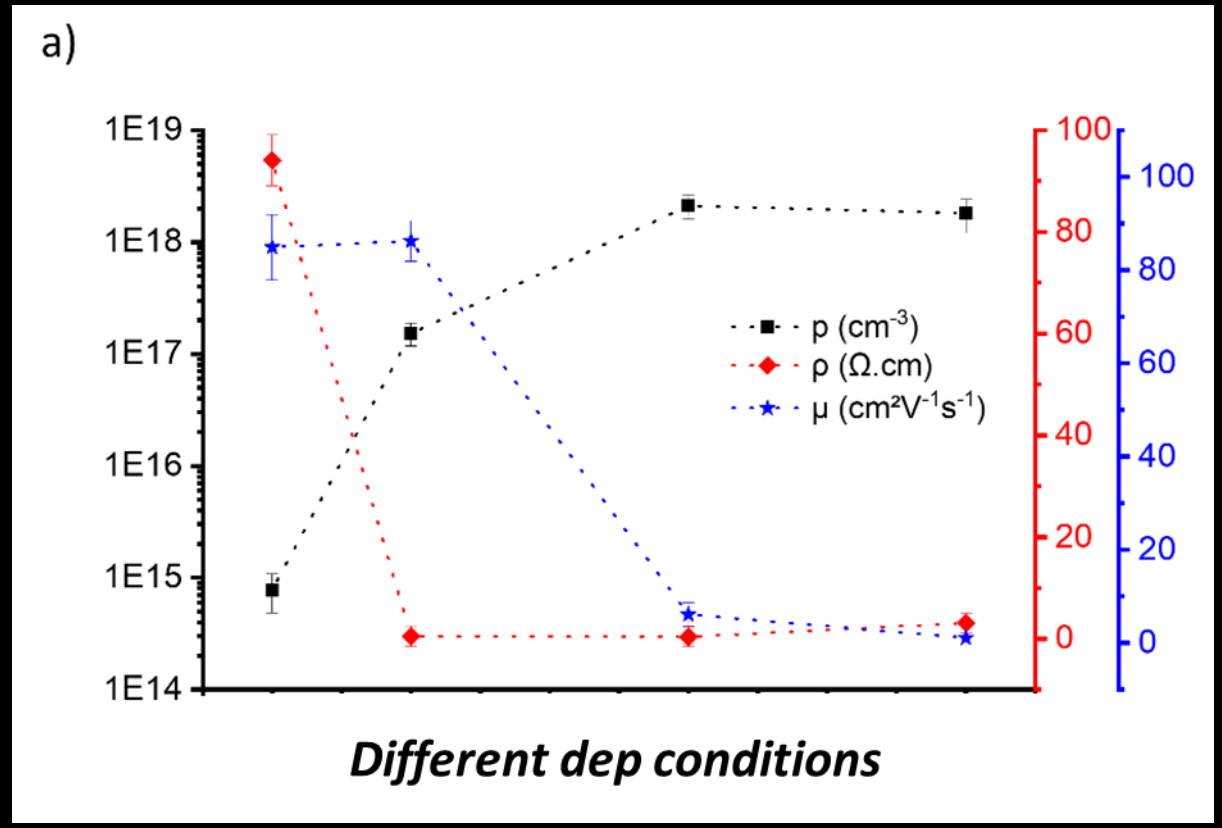


A. Sekkat, Nature ComMat 2021

Cu_2O from a "new" solid precursor

Even Further optimized, to be published

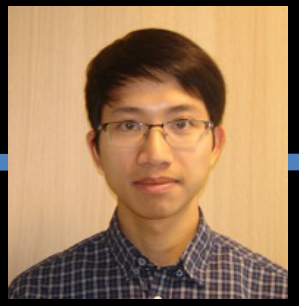




Record resistivity value for non epitaxial Cu_2O thin films, tunable transport properties

A. Sekkat, submitted

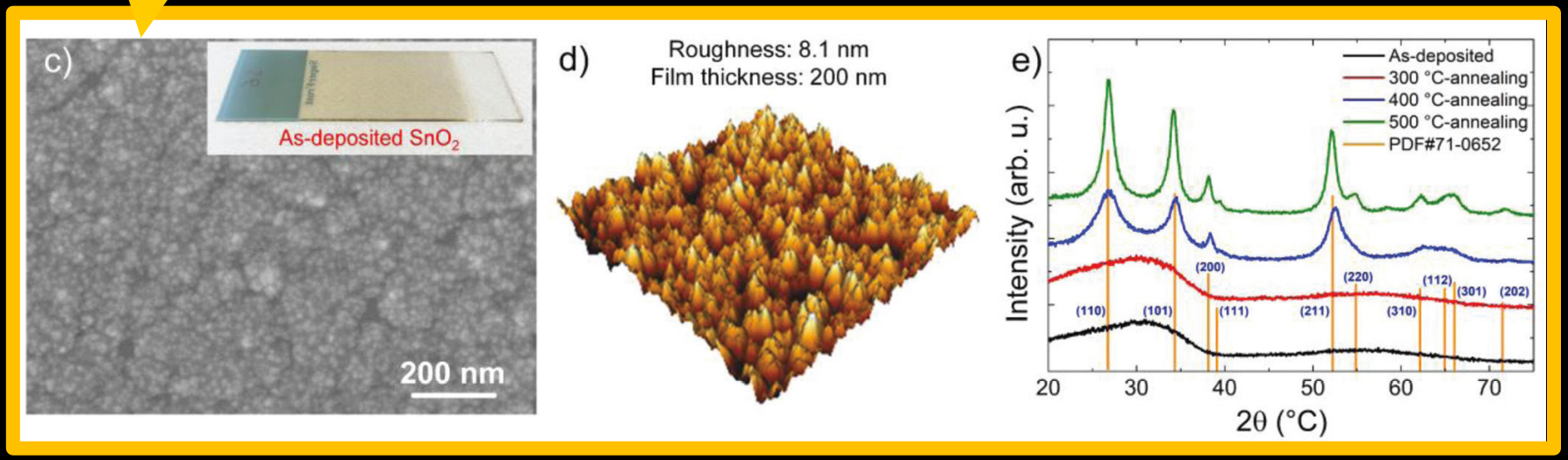
Open air deposition of SnO_2



Masoud Akbari *Viet Nguyen*

Different Sn precursors evaluated (DFT) and some tested:

$Sn(acac)_2$ and bis[bis(trimethylsilyl) amino] tin(II)



Hydrophpbic surface due to ligand adsorption : NO SnO_2 deposition

First demonstration of SALD deposition of SnO_2 from $Sn(acac)_2$, Key impact of open air processing and atm. Pressure on reaction output

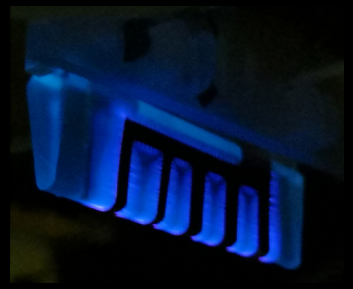
V. Nguyen, M.Akbari et al. Dalton Trnas. 2022, accepted

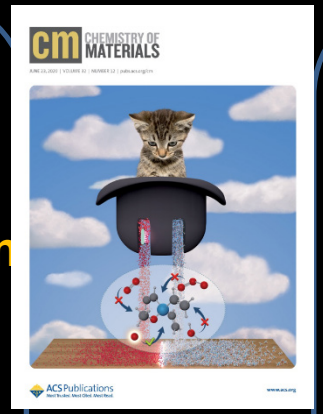
SALD Research at LMGP

SPECIFICATION OF THE SALD	
Deposition Temperature	RT to 350 °C
Deposition Area	1 to 25 cm^2
Growth rate	Up to 2 nm/Cycle
Subtrates	Metal, glass, plastic, tissue,
Maximum Achievable Thickness	Up to several µm

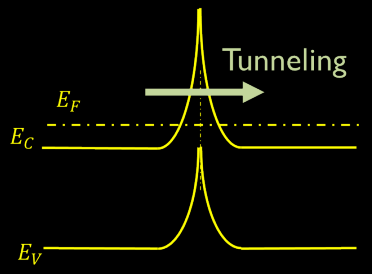
Materials available or in study:
ZnO, Al_2O_3, Al:ZnO, Cu, Cu_2O, CuO, TiO_2, SiO_x, MgO, SnO_2, Ga_2O_3, HfO_2, Ag, CeO_2, ZrO_2, Hybrids (Metalcones, MOFs, …)

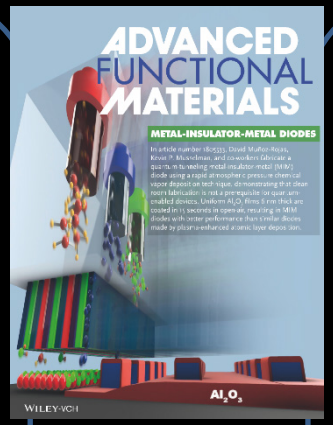
Design & Optimization
- Atm. Plasma activation
- up-scaling/simulation



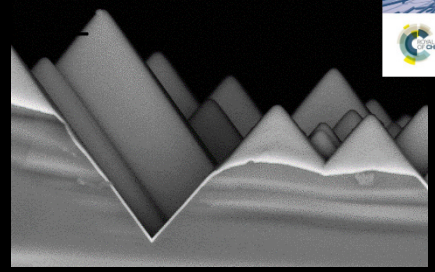


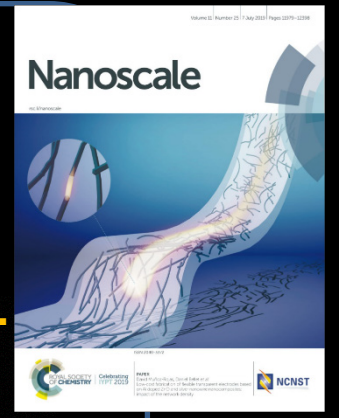
Fundamental studies
- Effect of open-air processing
- New materials





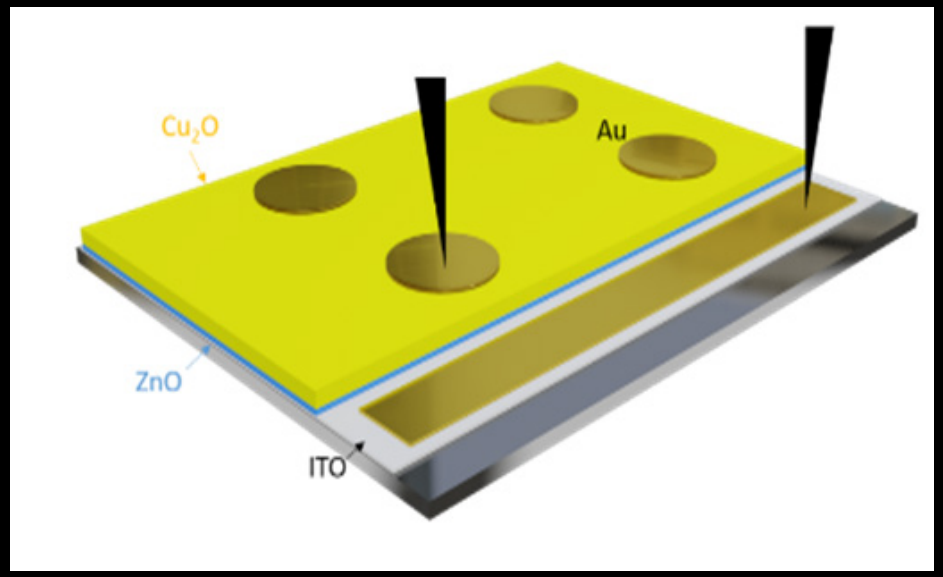
Applications
- TCM
- PV
- Sensors
- Res.Switc.

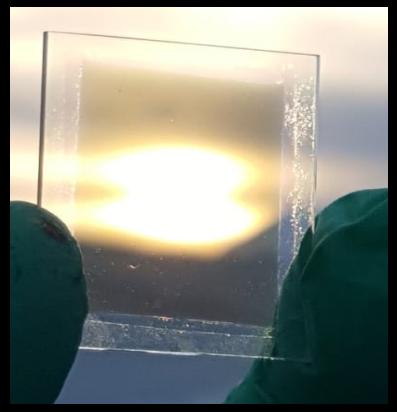


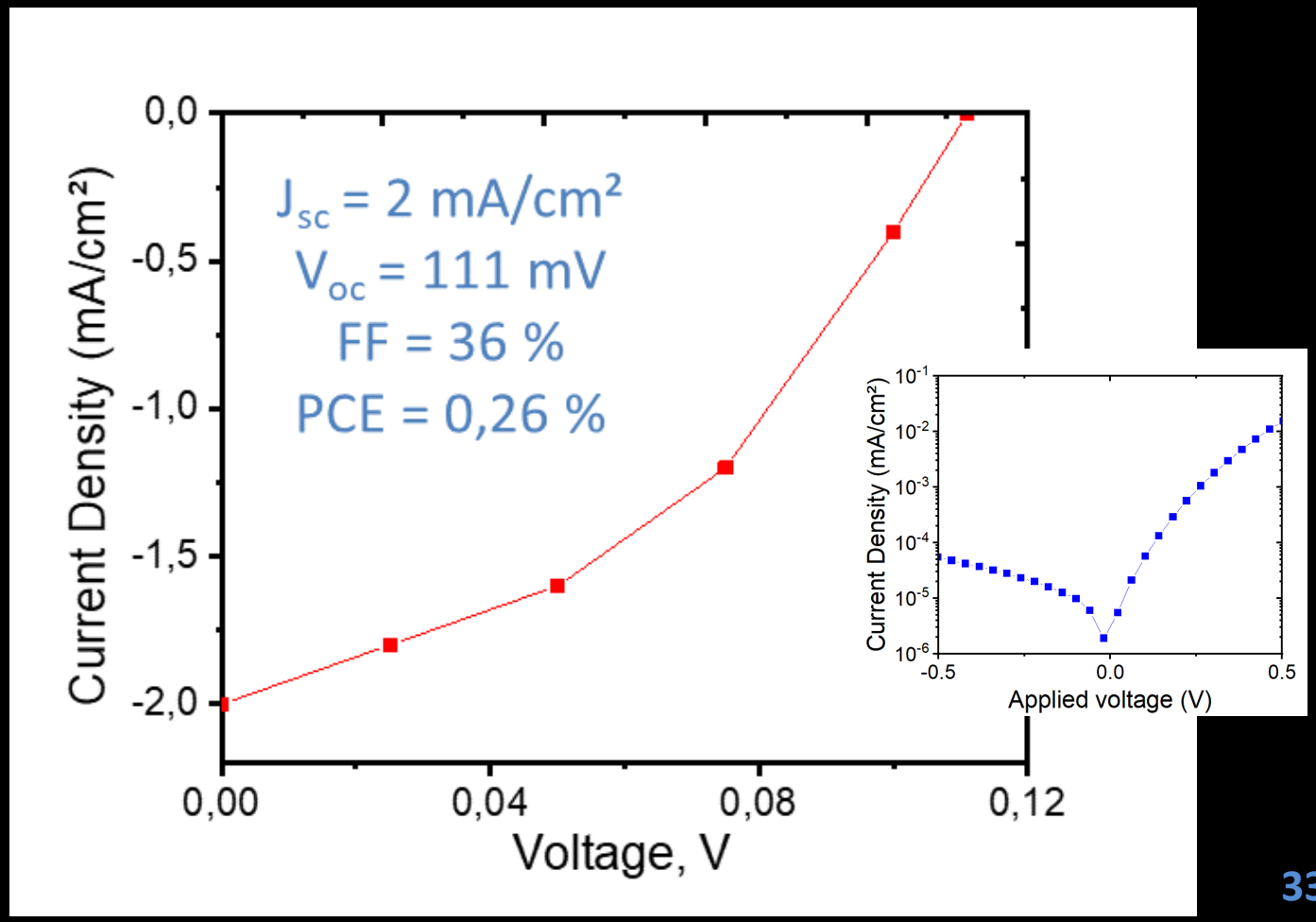


All-oxide solar harvester

Ultra-thin ZnO/Cu_2O by SALD at low temperature







Abdou Sekkat

A. Sekkat, Nature ComMat 2021

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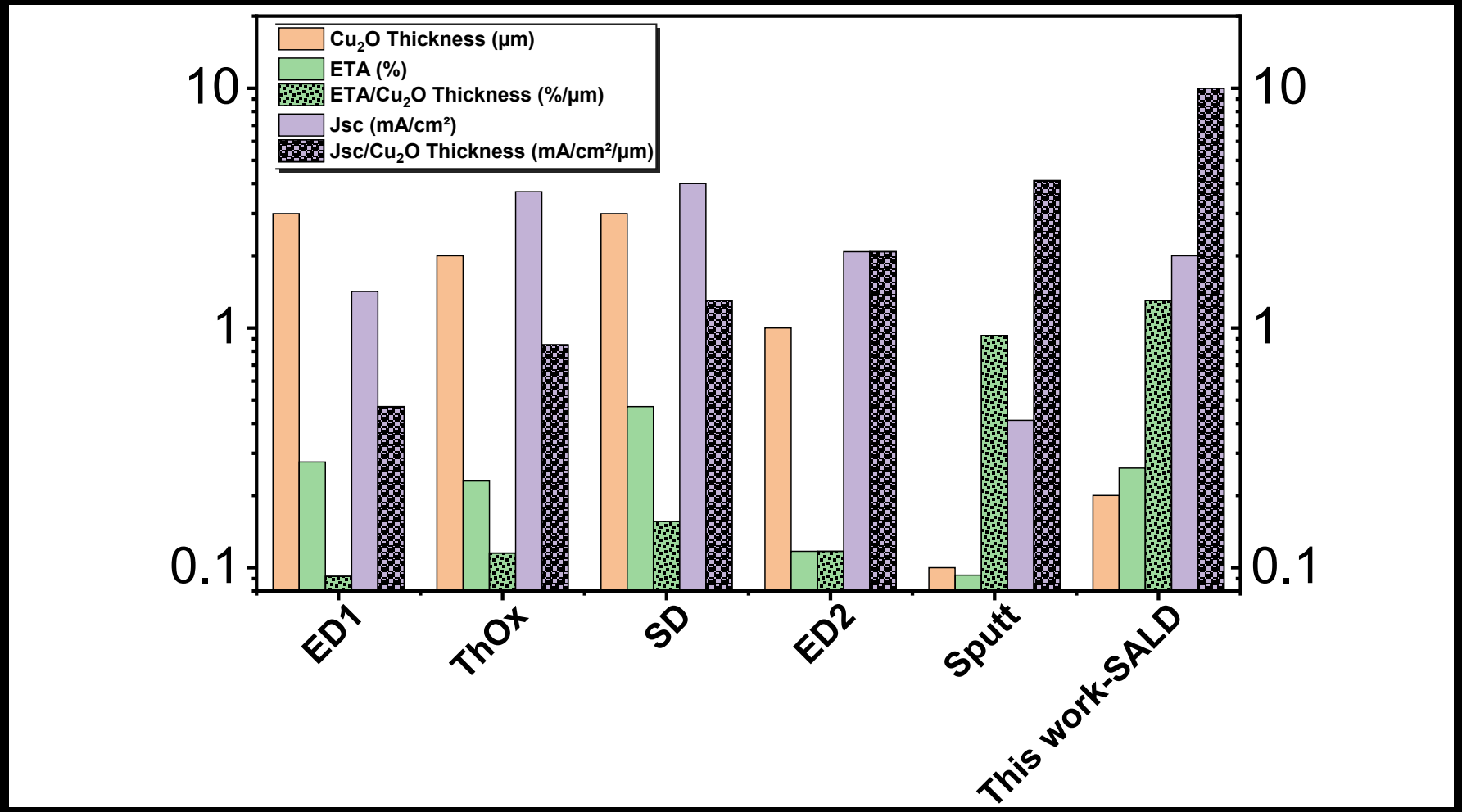
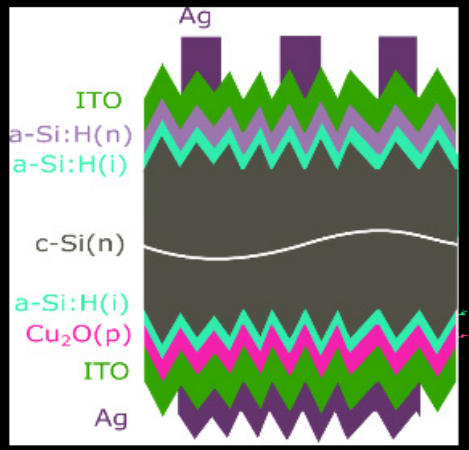


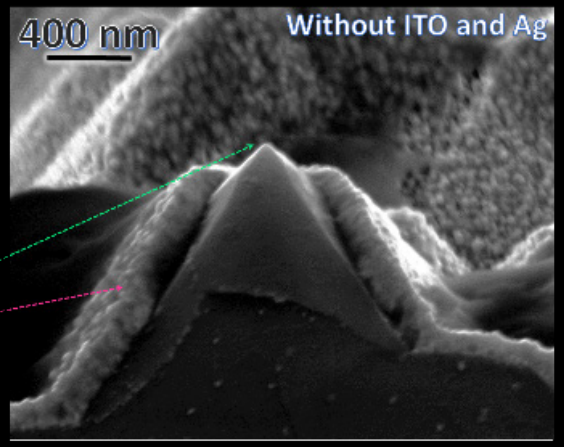
Atmospheric, low-temp. Fabrication of semitransparent Cu_2O devices with efficiency comparable to much thicker devices

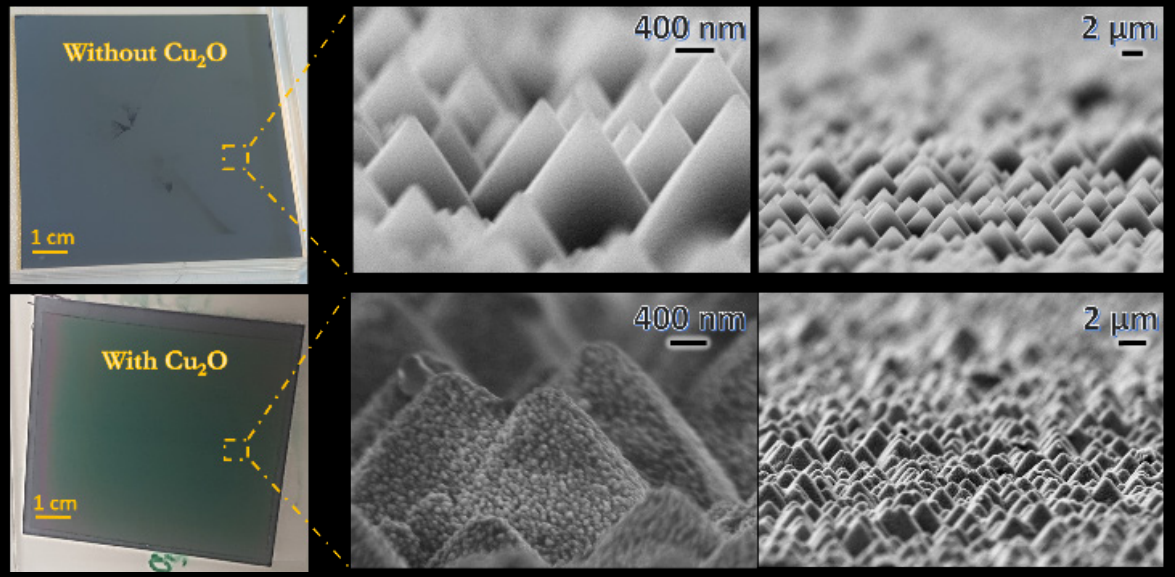
A. Sekkat, Nature ComMat 2021, vol 2 article 78

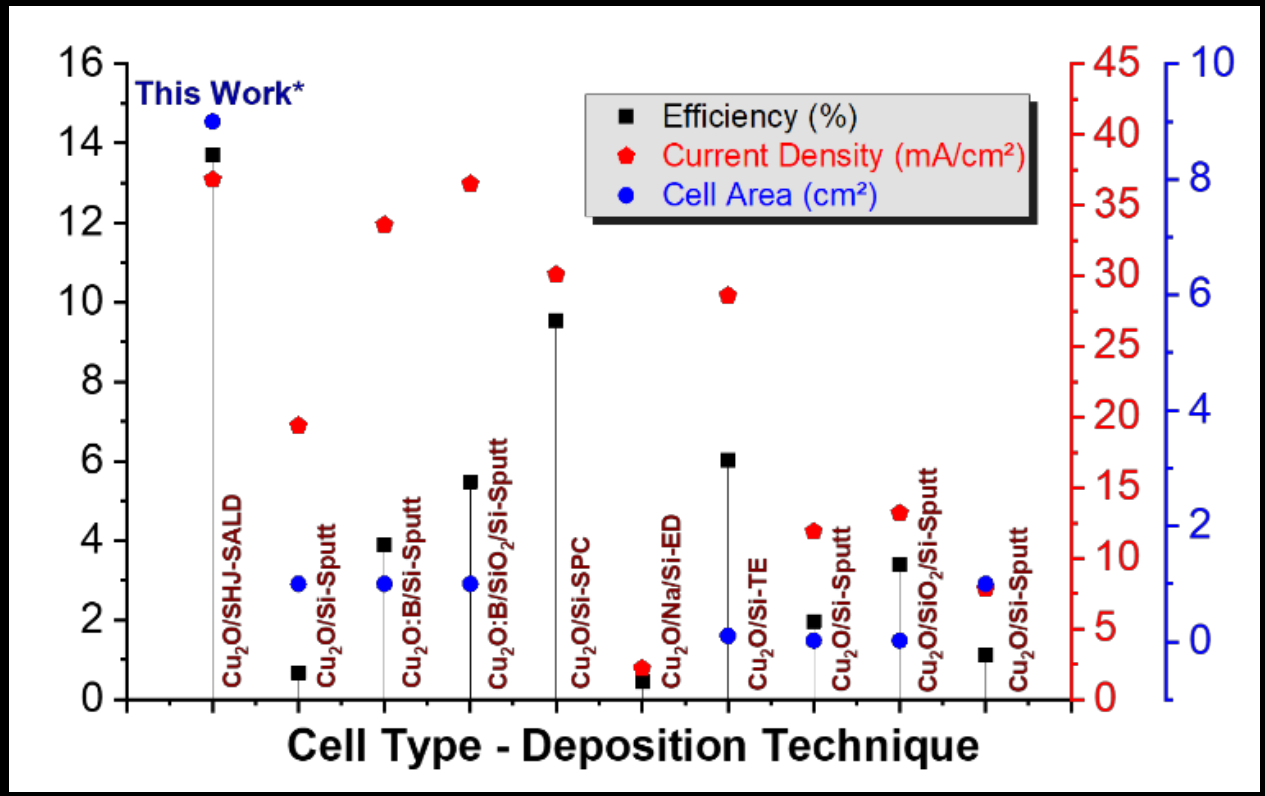
Cu_2O for Photovoltaic applications

Cu_2O for HET cells, coll INES









J.Mater. Chem. A, 2021

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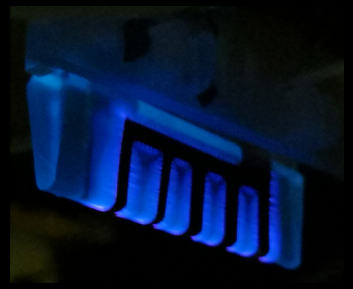

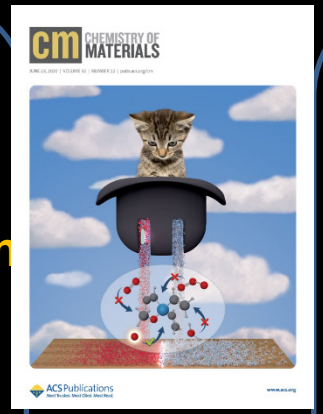

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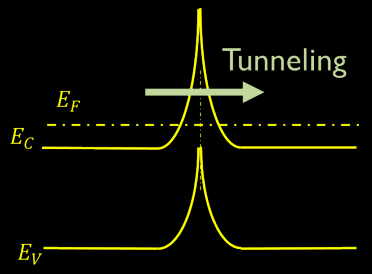

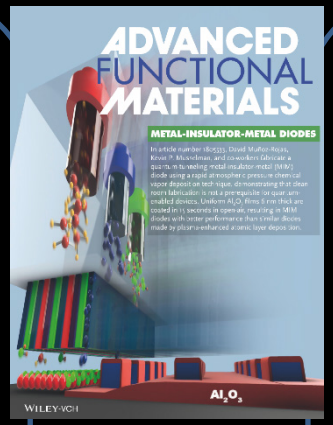

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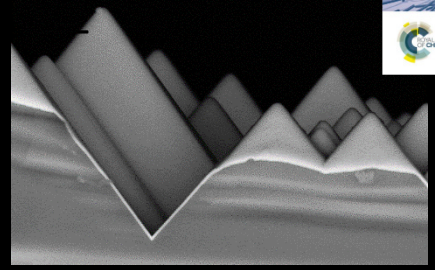

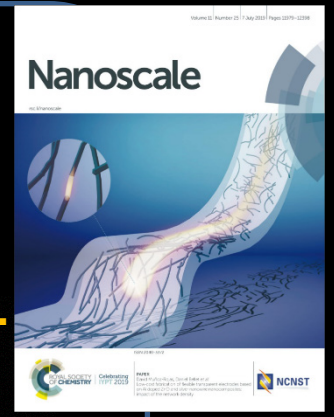

We are recruiting PhDs and Postdocs

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http://sites.google.com/site/workdmr/

Thanks for your attention!!!