LMGP

Critical materials & environmental impacts:

ongoing works…

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cnrs dépasser les frontières

Introduction – ZnO and its assets

LMGP

o **Compound semiconductor (vs Si, Ge)**

- no toxicity, biocompatibility
- relatively abundant elements (EU CRM, USGS, …) & low-cost

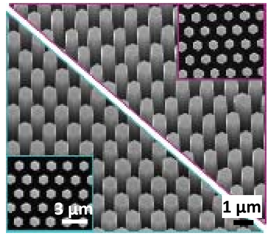
o **Fabrication process :**

- low-temperature, low-cost chemical deposition techniques
- compatibility with green chemistry to some extent
- scaling-up to high surface area
- industrial compatibility

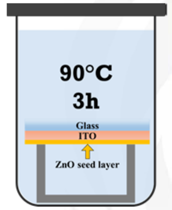
o **Attractive properties:**

- wide band gap energy: 3.37 eV at RT
- large exciton binding energy: 60 meV / GaN
- high electron mobility: 200 $cm^2V^{-1}s^{-1}$ / TiO_2
- large piezoelectric constants: d_{33} = 12.3 pC/N / AlN
- nanostructures with different shapes
- typical dimensions of ZnO nanowires:

diameter: 30 – 80 nm & length: 300 nm – 10 µm



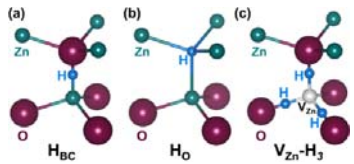
ZnO nanowires

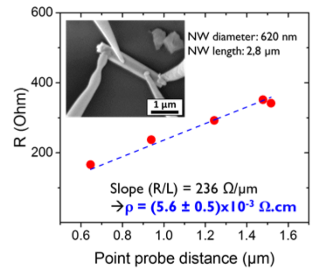


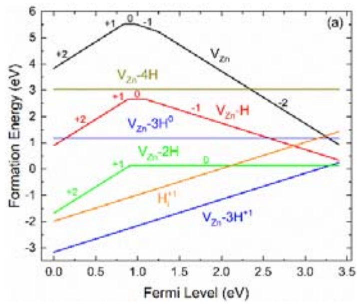
CBD

MOCVD

ALD







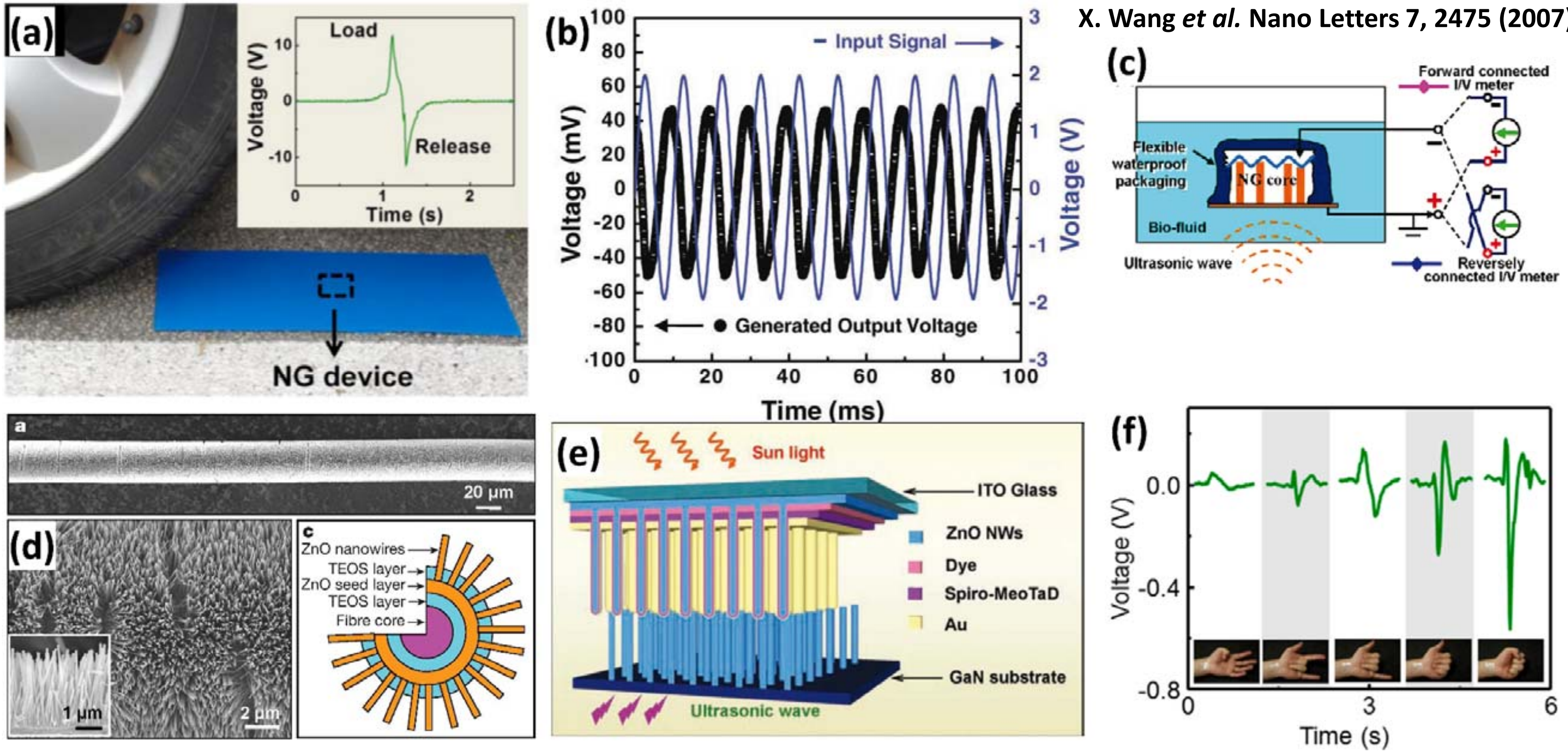
Activity start in 2010 (12 PhD thesis)
→ chemical synthesis & in the structural characterization

different applications in the field of energy

Introduction – nanowire-based piezoelectric devices

Vertically Integrated Piezoelectric Devices made of semiconducting nanowires

L. Lin *et al.* Nano Energy 2, 75 (2013) S.N. Cha *et al.* Advanced Materials 22, 4726 (2010) X. Wang *et al.* Nano Letters 7, 2475 (2007)

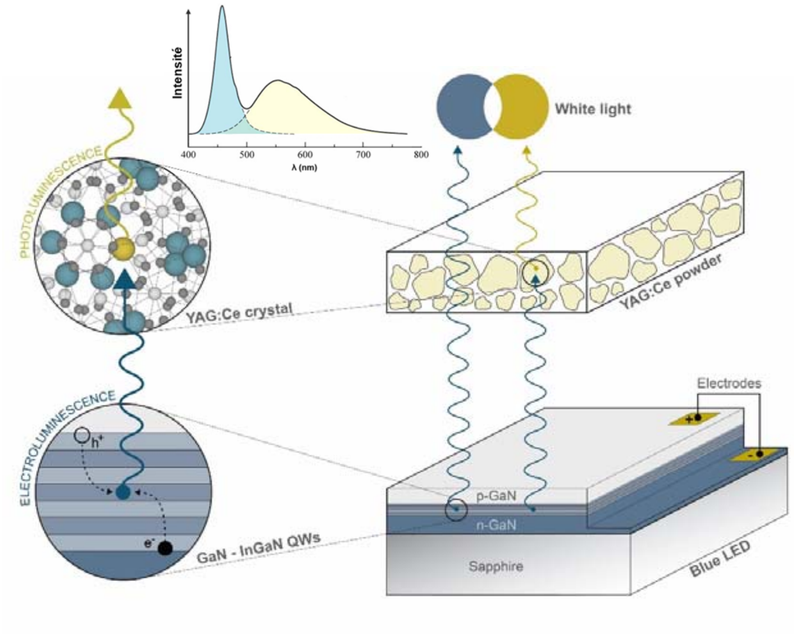


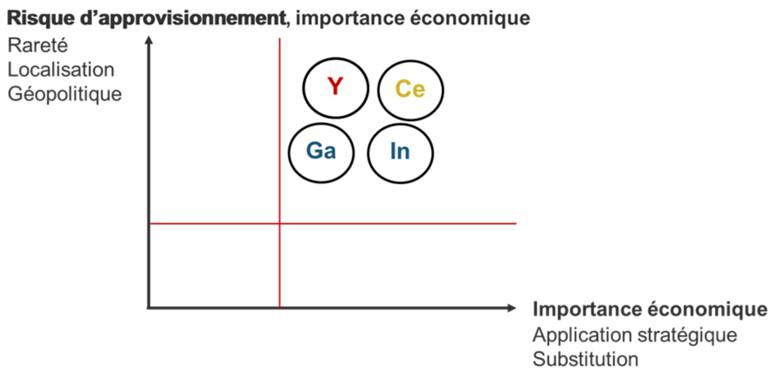
Y. Qin *et al.* Nature 451, 809 (2008) C. Xu *et al.* Advanced Materials 23, 873 (2011) K.C. Pradel *et al.* Nano Letters 14, 6897 (2014)

V. Consonni *et al.* Nano Energy 83, 105789 (2021)

An Example of Interdisciplinary Research

Pierre Gaffuri





Couche 2 : Luminophore

Grenat d'aluminium et d'yttrium dopé au cérium (YAG:Ce)

(eQY > 70 %)

Couche 1 : LED bleue

Nitrure de gallium et d'indium (GaN-InGaN)

(eQE > 70 %)

Matériaux critiques

European Commission, Study on the EU's list of Critical Raw Materials (2020)

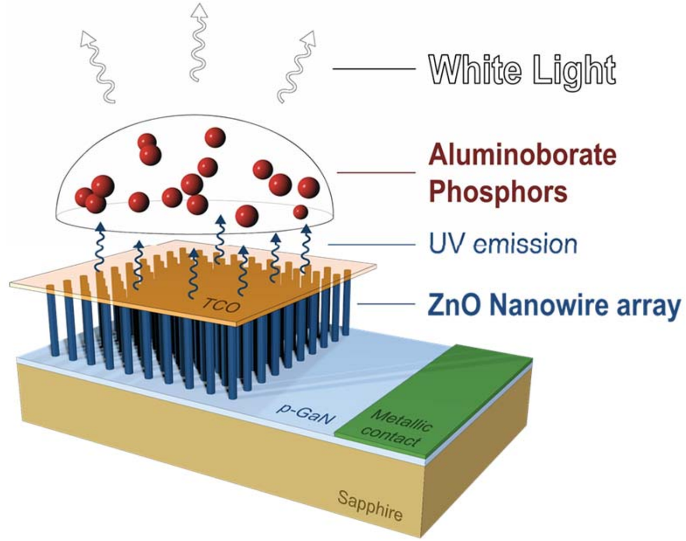
USGS. Mineral Commodity Summaries 2020. U.S Department of The Interior, (2020).

P. Gaffuri, E. Stolyarova, D. Llerena, E. Appert, M. Consonni, S. Robin, and V. Consonni, Renewable & Sustainable Energy Reviews 143, 110869 (2021)

An Example of Interdisciplinary Research

	Blue LED		Yellow emitting phosphor	
	Ga	**In**	**Y**	**Ce**
Materials in pc-wLED	GaN (>99 %)	InGaN (<1 %)	YAG (>99 %)	Substituting <1 % of Y atoms in YAG
Role in pc-wLED	Transports electrons to InGaN layers	Creates blue photon	Suitable matrix to host Ce atoms	Converts blue photon into yellow photon
	Economic importance			
Economic importance index *Criticality threshold=2.8*	**3.2**	**3.1**	**3.2**	**3.2**
Main application *(% for lighting)*	Integrated circuits 70% *(25%)*	Transparent conductive oxide 60% *(3%)*	Phosphors for lighting *46%*	Catalyst 35% *(1%)*
Refinery production *(tonnes/year)*	320 *(USGS)*	760 *(USGS)*	10 000 - oxide *(USGS)*	51 000 *(UE)*
	Supply risks			
Supply risks index *Criticality threshold=1*	**1.4**	**2.4**	**3.8**	**5.7**
Estimated reserves *(tonnes)*	< 100 000 *(USGS)*	18 800 *(EU)*	> 500 000 - oxide *(USGS)*	9 600 000 - oxide *(USGS)*
Herfindahl-Hirschman-Index *(HHI)*[1]	3.5	2.5	9.2	
Avg concentration in exploited ores	50 ppm (Bauxite) *(USGS)*	1–100 ppm (Zinc-sulfide ores) *(USGS)*	300 ppm to 2% of mixed RE *(USGS)*	
Recycling rate *(End of life)*	0% *(EU)*	0% *(EU)*	Insignificant *(USGS)*	

understanding the criticality of Ga, In, Y, Ce and their role in the LEDs…



Pierre Gaffuri

Alternative technologies to reduce & substitute critical materials in LEDs

Table 4
Willingness-to-Pay for the different attributes.

	Willingness to pay (WTP)	
Prices	€10	€15
Preferred color	1.93	0.74
Without CM	2.82	1.09
Low vs High impact	3.93	1.52
Medium vs High impact	2.74	1.06
Electrical consumption	−0.28	−0.11

Choice experiments to assess the consumer behavior

P. Gaffuri, E. Stolyarova, D. Llerena, E. Appert, M. Consonni, S. Robin, and V. Consonni, Renewable & Sustainable Energy Reviews 143, 110869 (2021)

What Next ! – Criticality vs Performances

ZnO is composed of Zn and O, but additional elements named dopants are required to enhance its properties

Al Ga Cu Sb

a common way to modulate the electrical conductivity of ZnO and/or its activity to name a few

Table 5: 2020 Critical raw materials for the EU

2020 Critical Raw Materials (30)			
Antimony	Fluorspar	Magnesium	Silicon Metal
Baryte	Gallium	Natural Graphite	Tantalum
Bauxite	Germanium	Natural Rubber	Titanium
Beryllium	Hafnium	Niobium	Tungsten
Bismuth	HREEs	PGMs	Vanadium
Borates	Indium	Phosphate rock	Strontium
Cobalt	Lithium	Phosphorus	
Coking Coal	LREEs	Scandium	

Supply Risk index > 1 & Economic Importance index > 2.8 → the idea is to go beyond the traditional indexes (geology, history, …)

assessing in the same investigation i) the criticality of Zn, Al, Ga, Cu and Sb and ii) the need for their use in order to improve the properties of ZnO → criticality vs performances (trade-off!!!)

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Présentation of Hugo & Adrien

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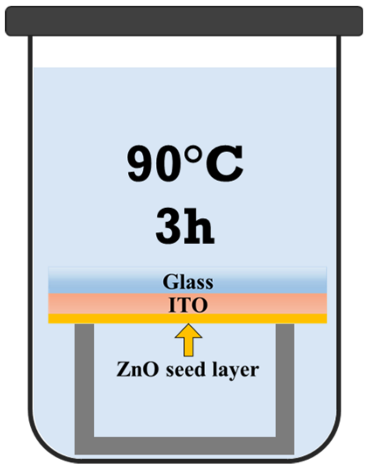
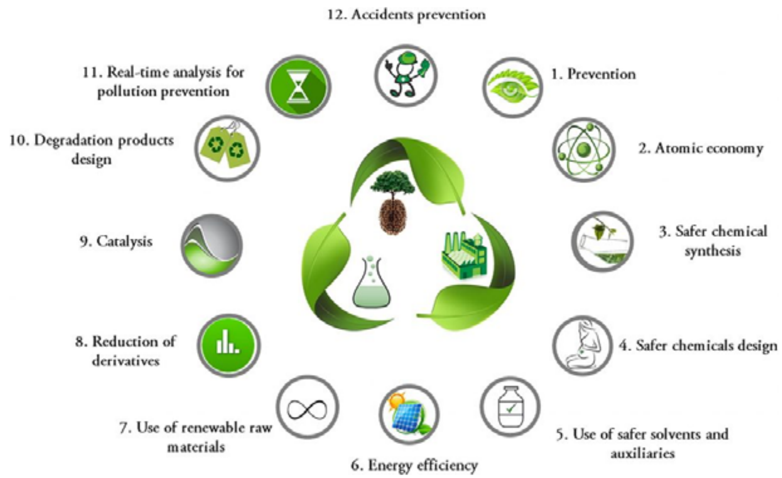
What Next ! – Reduction of Environmental Impact vs Performances



ZnO nanowires grown by chemical bath deposition*

- Low cost and easily implemented process
- Low temperature < 100°C (flexible substrate)
- Surface scalable for industrial purposes
- Compatible with green chemistry

solvent: deiniozed water
chemical precursors: zinc salt + **HMTA** (+ NH_3)

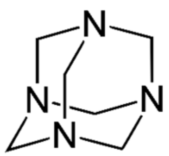


Schematic of the 12 principles of green chemistry

P. Anastas *et al.* Chem. Soc. Rev. 39, 301 (2010)

$Zn(NO_3)_2$ → produces Zn(II) species

HMTA



→ acts as a pH buffer &
→ gradually releases OH^- ions but also formaldehyde…
→ acts as a capping agent to inhibit the radial growth
→ affects the nucleation process on the seed layer

assessing how the properties of ZnO are affected by the suppression of a chemical precursor as a mean to reduce the environmental impact of the fabrication process

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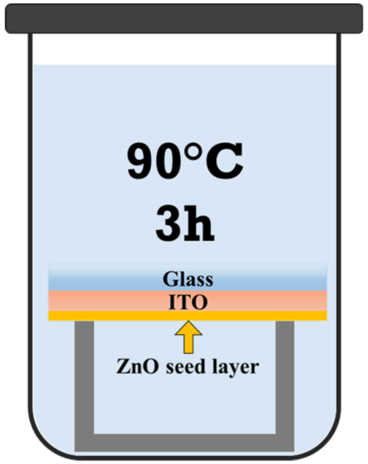

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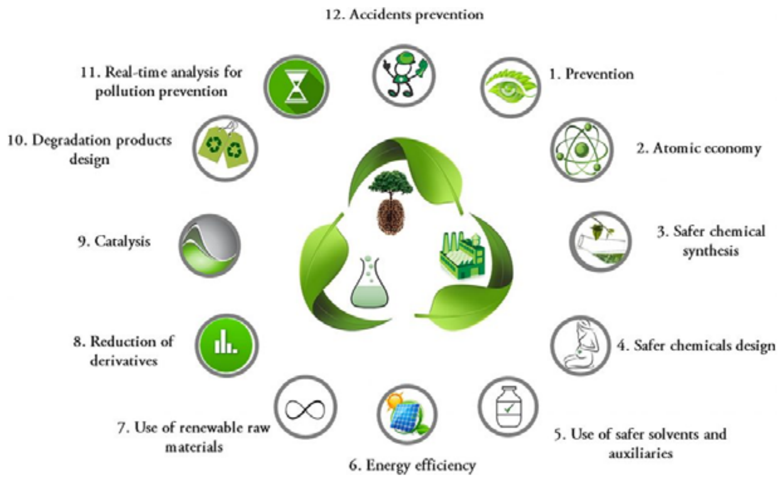

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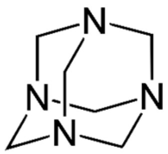

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→ ***Presentation of Adrien***

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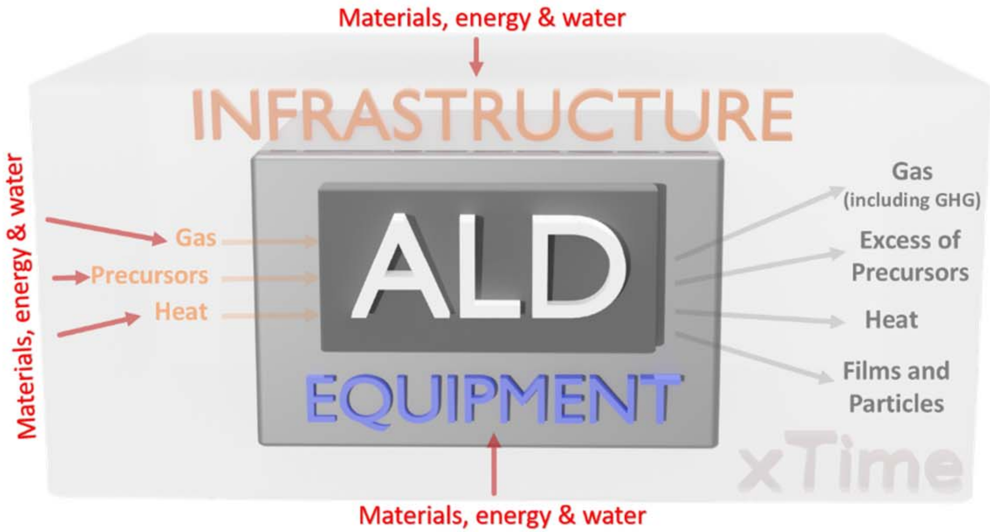
What Next ! – Reduction of Environmental Impact vs Performances

The **assessment of the environmental impacts** associated with chemical deposition techniques is crucial to:

- help detecting their main sources of pollution.
- find paths towards their reduction, which is environmentally but also economically relevant.

→ Life Cycle Assessment is a powerful tool



Schematic representation of the environmental impacts associated to ALD processes.

- ***Software: Simapro***
- ***Database: Ecoinvent , calculation recipe midpoint***

reducing the environmental impact of the fabrication process while maintaining the performance of materials

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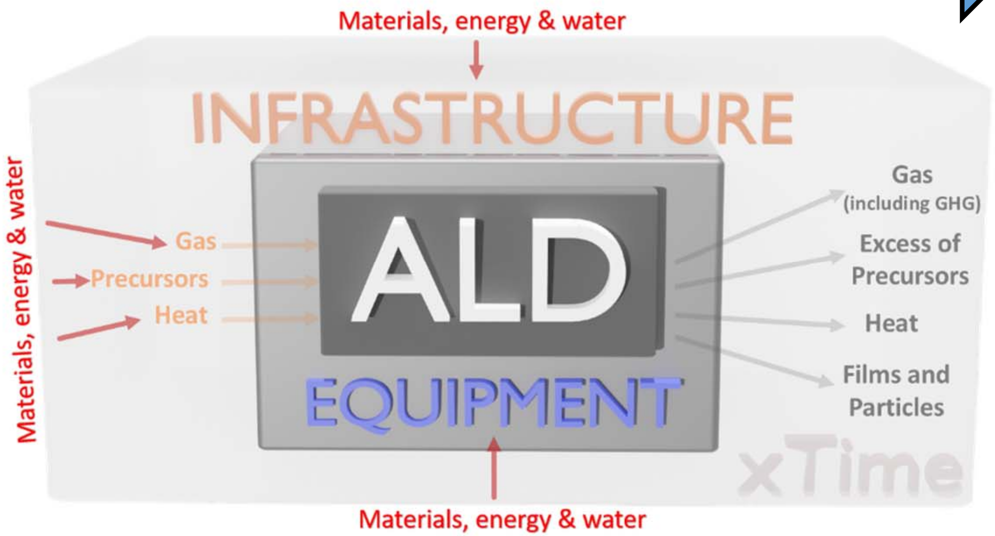
Activity of Matthieu



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THANK YOU FOR YOUR ATTENTION