NanoSen-AQM

Nanostructured gas sensors for the detection of air pollutants

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Centre National de la Recherche Scientifique

GT2 Development, characterization and fabrication of nanostructured gas sensors

Participants

CNRS CIRIMAT	
CSIC ITEFI	
CNRS LAAS	
UEX	

Specific Objective

O1	To reduce energy consumption and fabrication cost and to improve detection properties of gas sensors

Main Product

P2.1	Prototypes of nanosensors for the detection of target pollutants

Outline

Multisensor platforms

- MEMS technology
- Platform used

Sensing Materials

- SnO_2 / Electrospinning
- Graphene / Electrospray
- ZnO:Ga / RF sputtering

Sensing Results

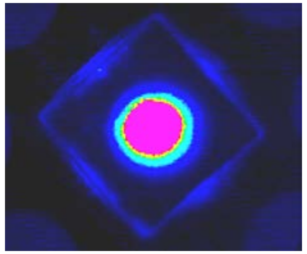
Conclusions

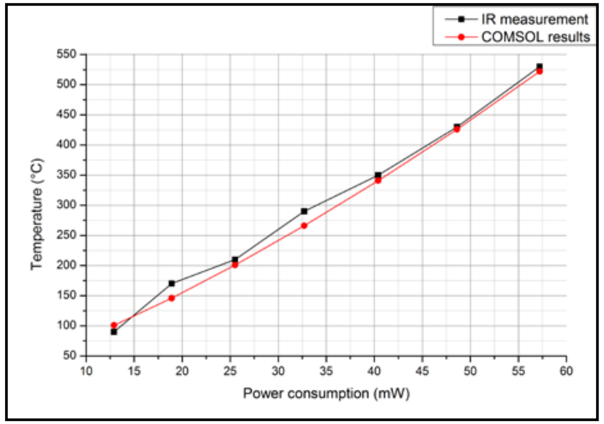
Product P2.1

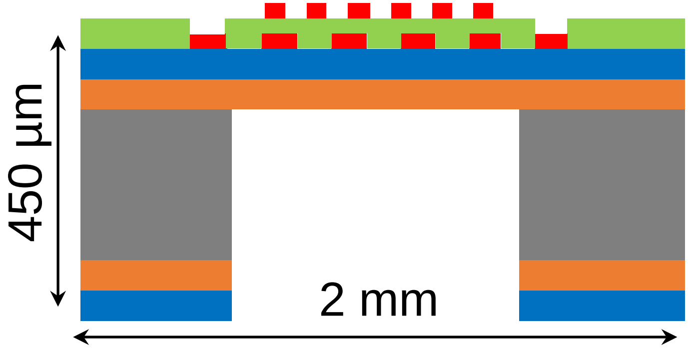
Multisensor platform

Micro-hotplates prepared by MEMS technology (LAAS CNRS)

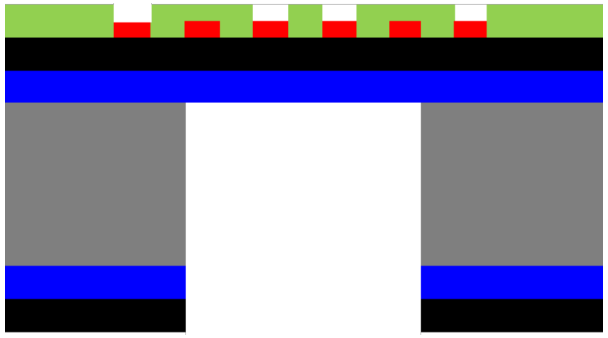
- High temperature **(>500°C)**
- Low power consumption (few tens of mW)
- Good homogeneity
- Low level of residual stress
- Reliability



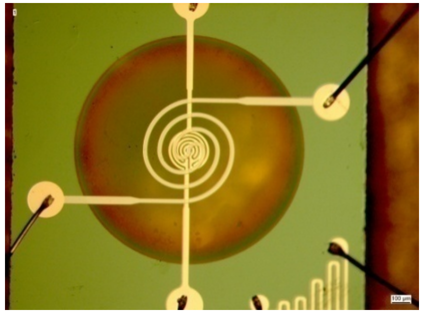




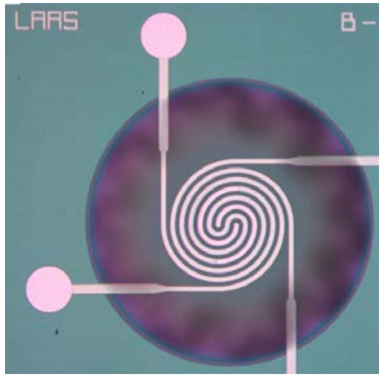
2 kinds of microhotplates



LAAS-CIRIMAT
ZnO:Ga sensors
(PVD : Sputtering)

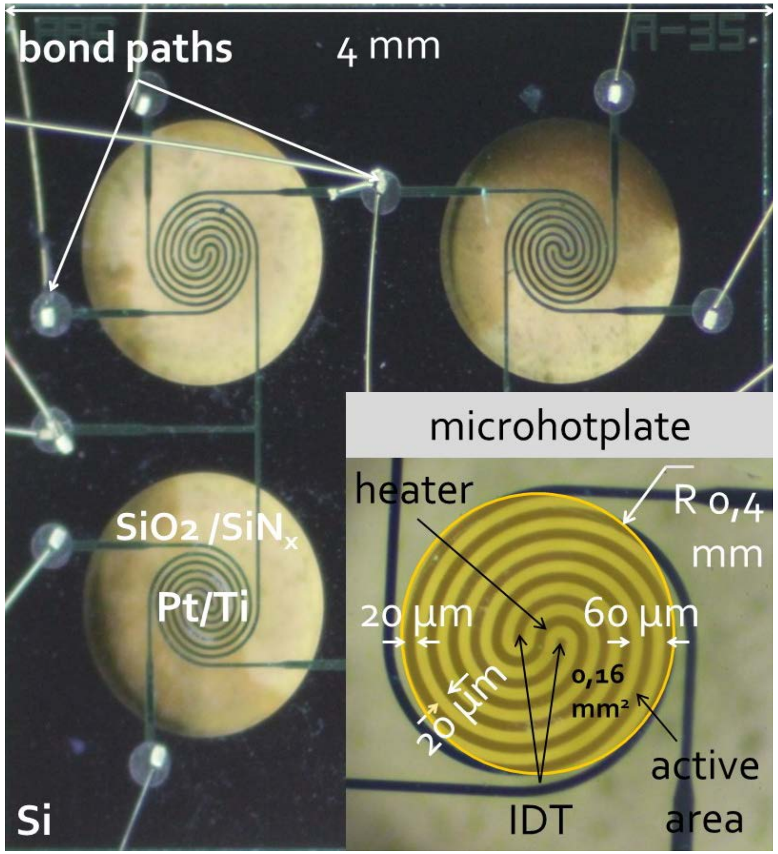


LAAS-CSIC
SnO2 Graphene based sensors
(Electrospinning)

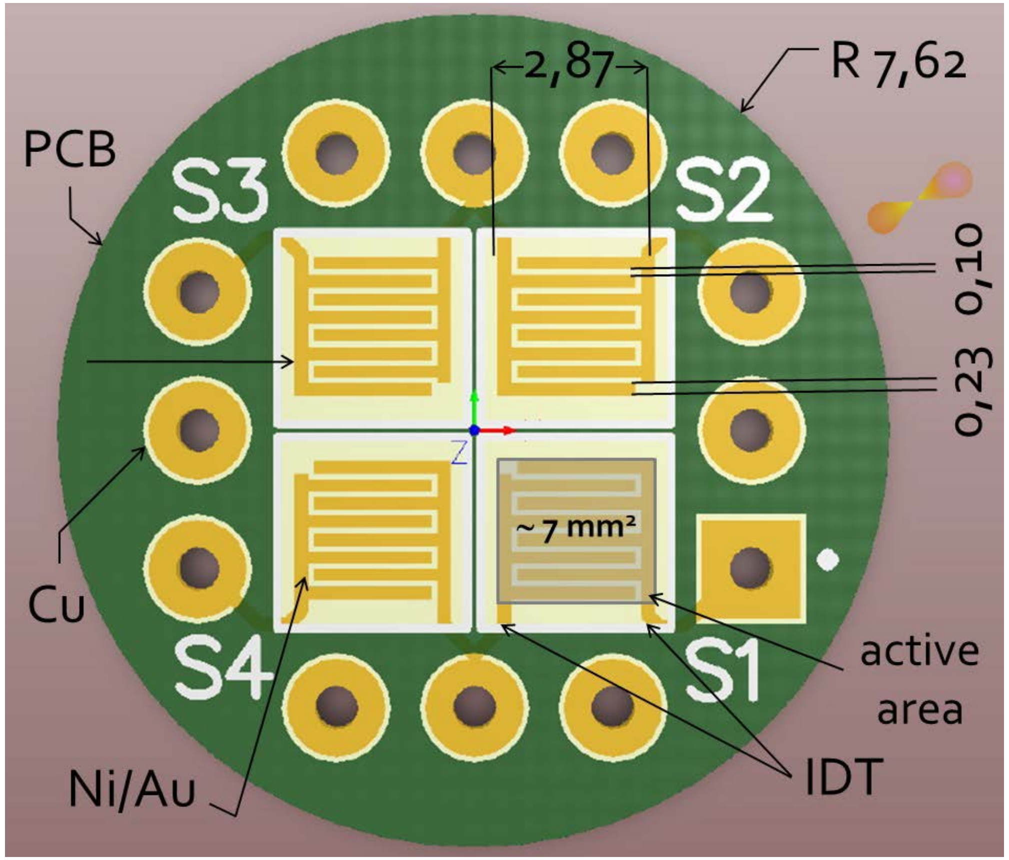


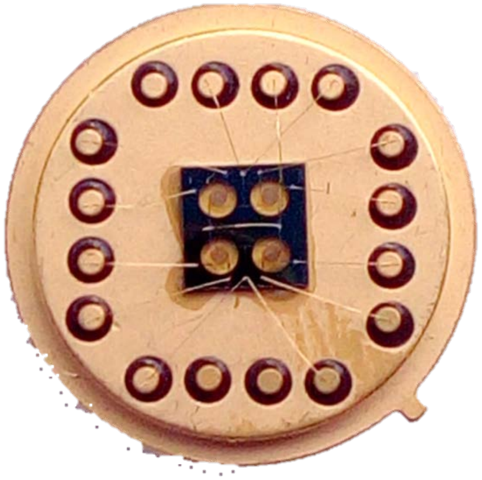
Multisensor platform

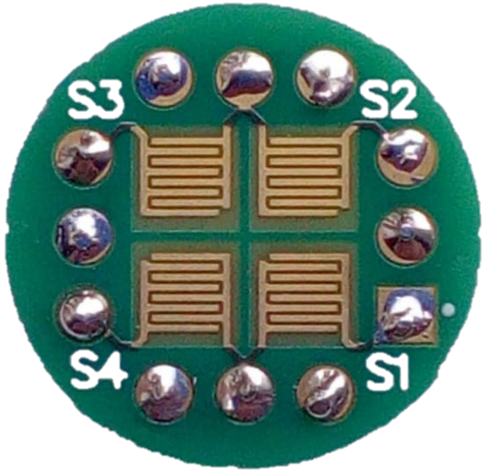
MEMS



Screen printing



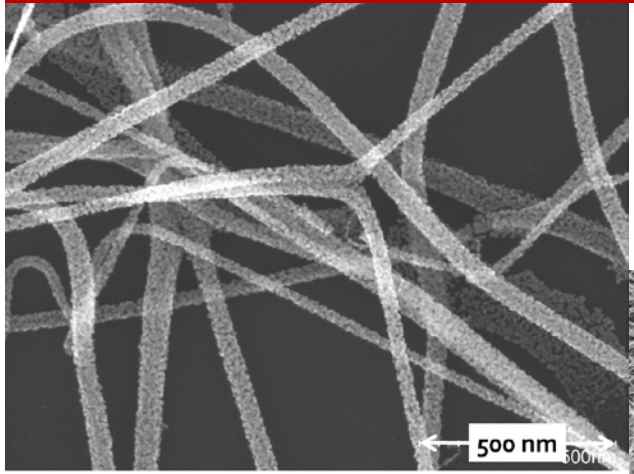




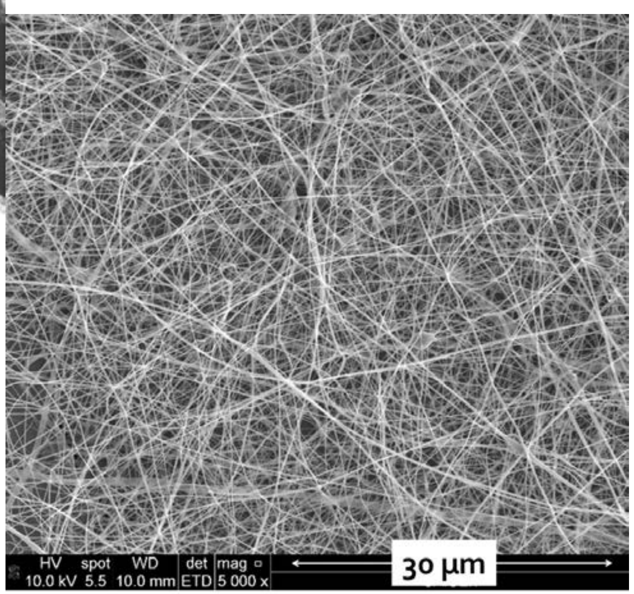
Sensing materials

Metal Oxide

Tin dioxide nanofibers — SnO_2 NF



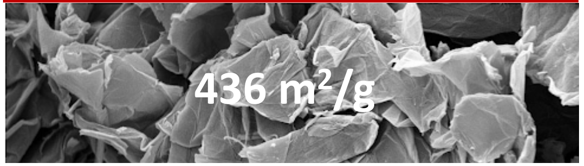
- Polycrystalline SnO2 (rutile)
- D_{fiber} ~ 10-50 nm
- L_{fiber} > 100 µm
- Granular surface
- D_{grain} < 10 nm
- Hollow fibers



- Highly porous web-like layer

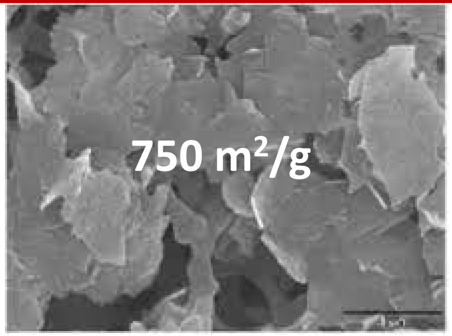
Graphene

Reduced graphene oxide rGO E800 (F)



Abalonyx
Innovative materials

Nanoplatelets XGnP (C)



XG sciences
THE MATERIAL DIFFERENCE

Sustainable mass production

Product	Maximum amount (g)	Price (€/g)
rGO E800	50	~ 20
XGnP	250	~ 0,7

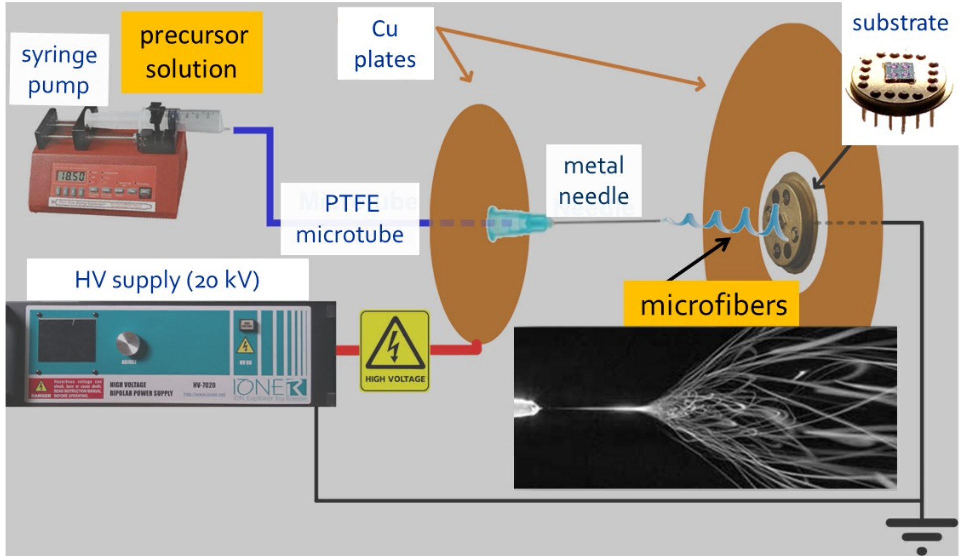
Sensing layer SnO_2 NF

1 Precursor solution

Compound	%wt.
DI water	80
Polivinil alcohol PVA	10
Tin chloride (IV) pentahydrate $SnCl_4 \cdot 5\ H_2O$	10

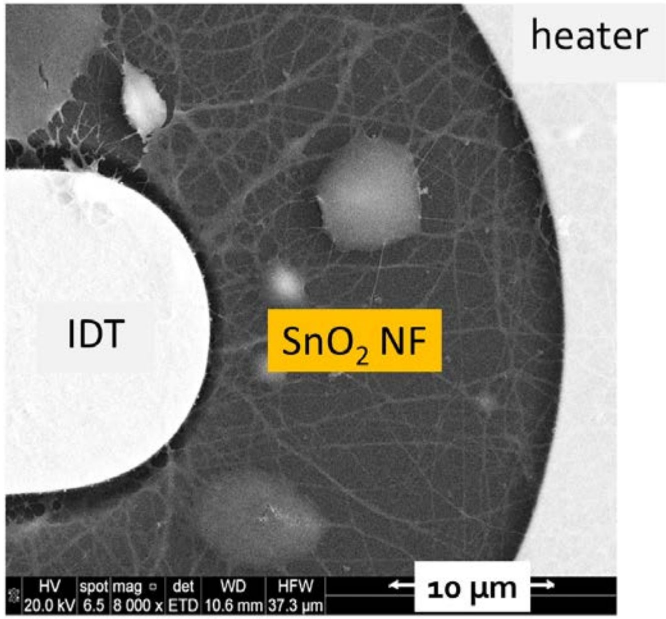
- Surface tension *(72 mN/m)*
- Viscosity *(0.6 Pa·s)*
- Conductivity *(30 S/m)*

2 Electrospinning -> nanofibers



- Needle diameter *(0.5 mm)*
- Electric field *(3 kV/cm)*
- Dosage rate *(2 µl/min)*

3 Calcination



- Temperature *(500 ℃)*
- Atmosphere *(air)*
- Duration *(4 h)*

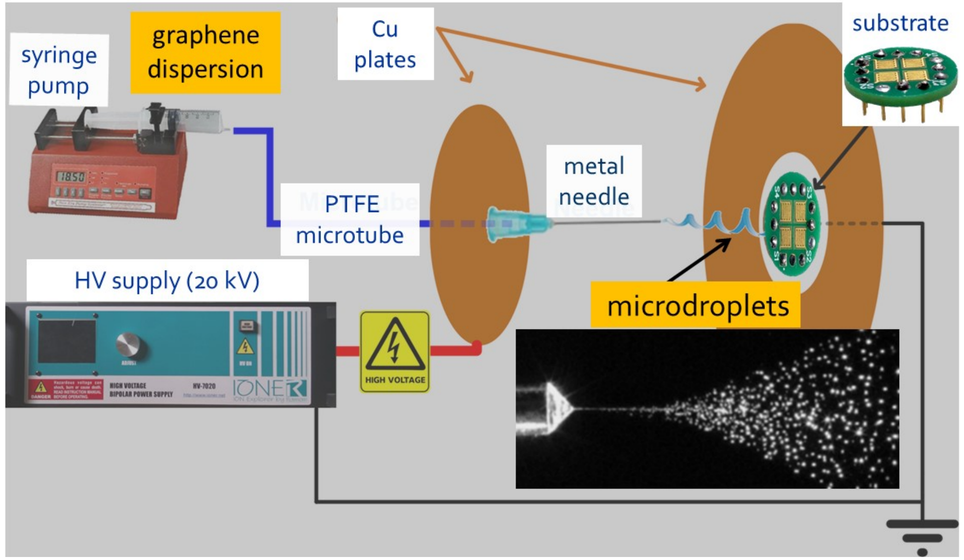
Sensing layer Graphene

1 Graphene dispersion

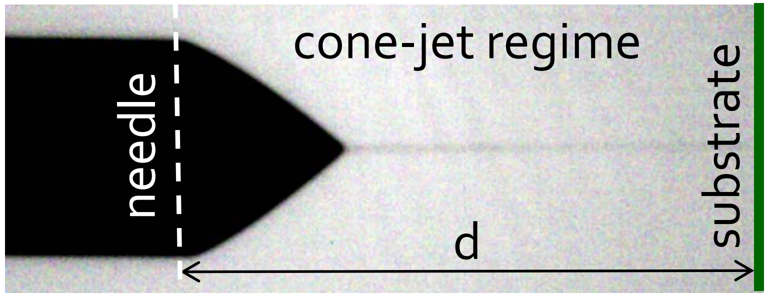
- Solvent *(IPA)*
- No surfactants/dispersants
- Concentration *(0.1 mg/ml)*
- Sonication time *(0.5-1 h)*

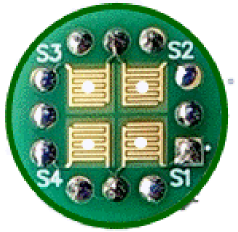
0.1 mg/ml
24h after sonication (1h)

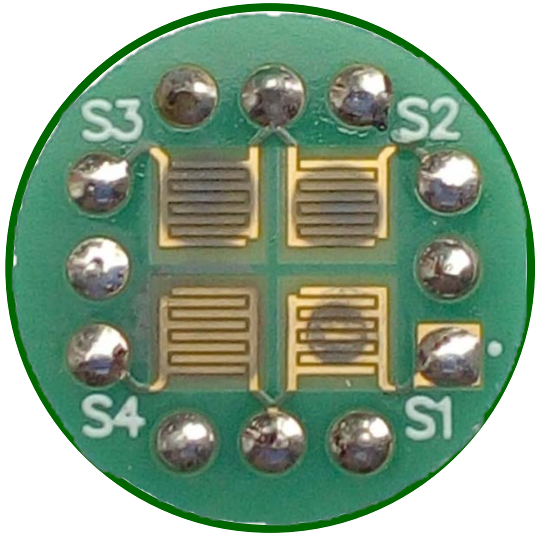
2 Electrospray



- Needle diameter *(0.5 mm)*
- Needle-substrate distance *(0.5-1 cm)*
- Electric field *(0.25-0.4 kV/cm)*
- Dosage rate *(2-5 µl/min)*
- Deposition time *(10-20 min)*





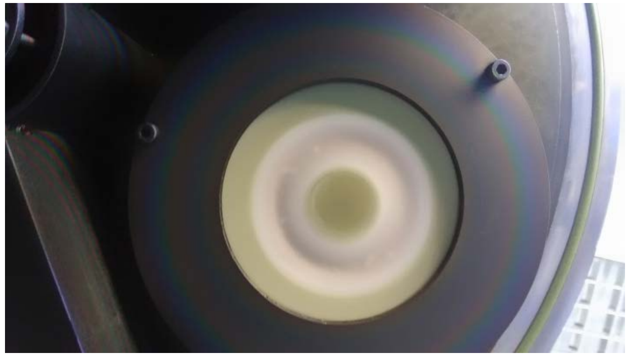


Sensing layer — ZnO:Ga thin films

1 Target preparation

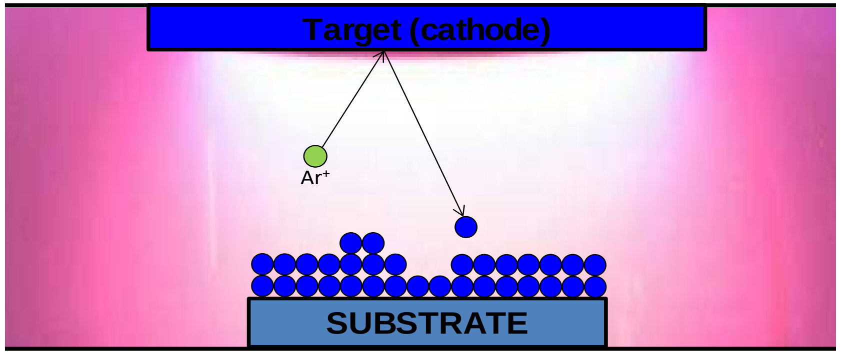
- $ZnO + 2$ %mol. Ga_2O_3
- *Pressing in a die (10 cm diam.)*
- Sintering at 1000 °C/ 5 h
- $Zn_{0.96}Ga_{0.04}O$

Target mounted on sputtering system



ZnO:Ga target

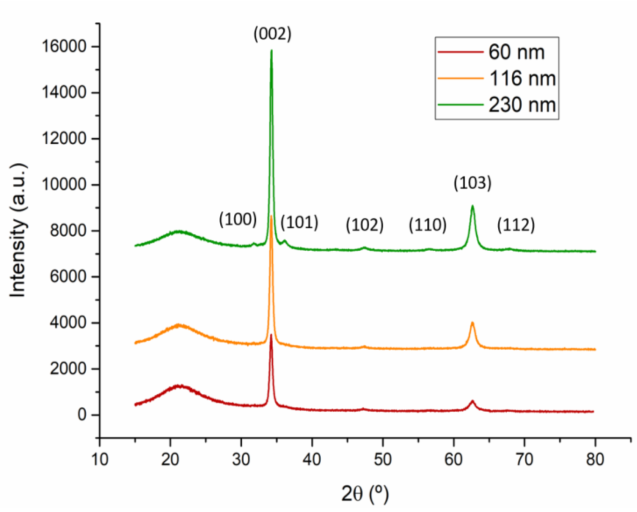
2 Sputtering deposition

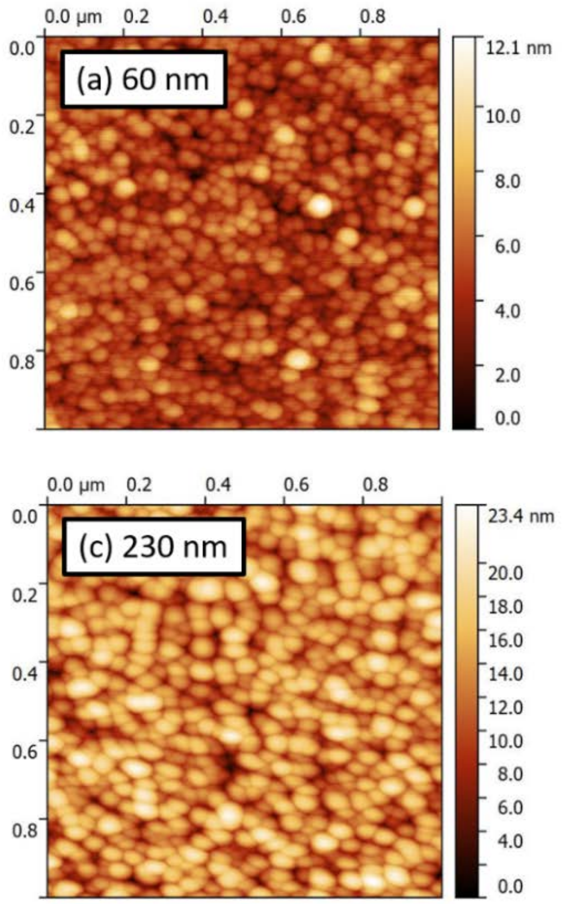


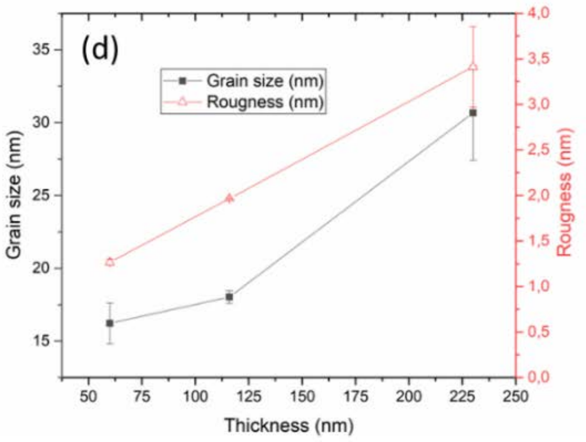
- Plasma process
- Ceramic target
- Pure Argon
- Magnetron sputtering
- Deposition rate *(~ 2 nm/min)*
- Deposition time *(12-100 min)*
- Thickness *(25-200 min)*

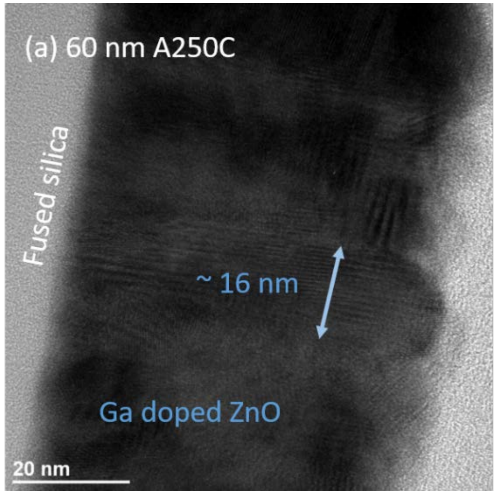
Sensing layer — ZnO:Ga thin films

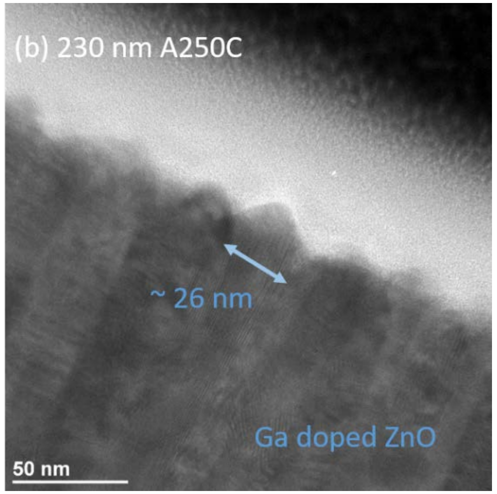
3 Microstructure









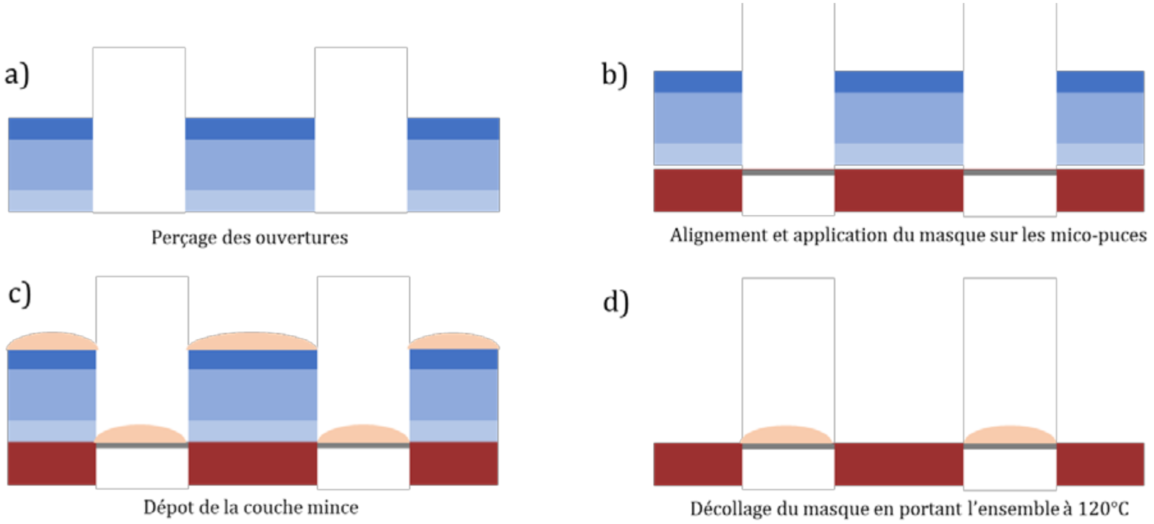


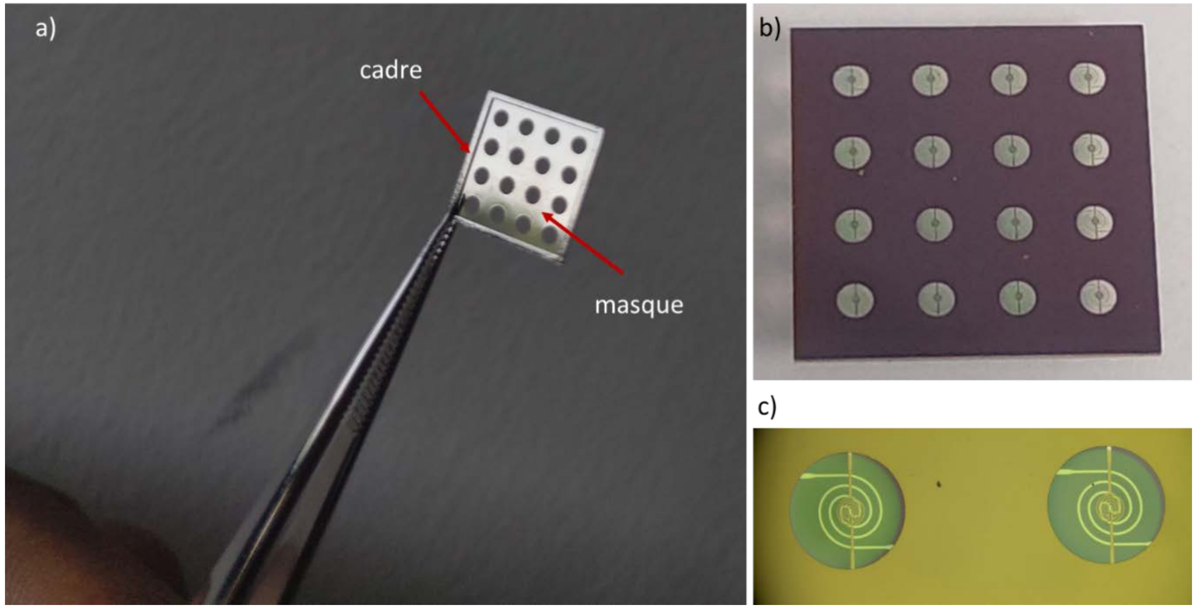
- Phase crystallization
- Nanosized grains
- Columnar structure
- Gallium inserted

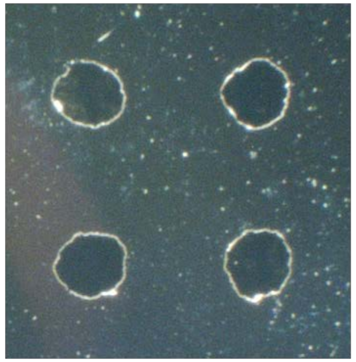
Layer integration

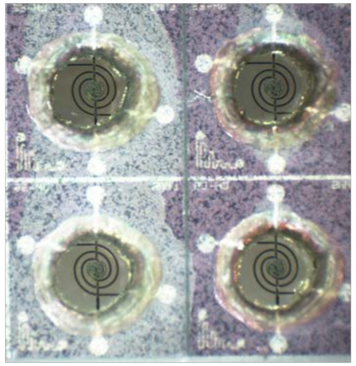
ZnO:Ga thin films

4 Integration

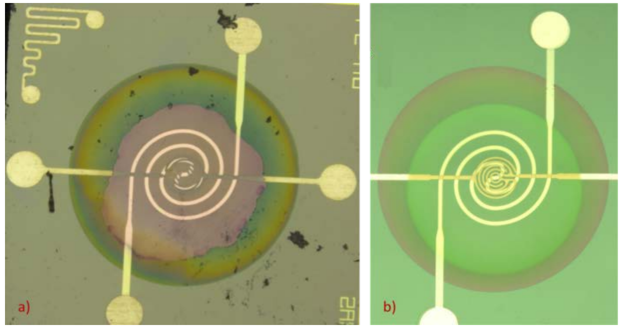


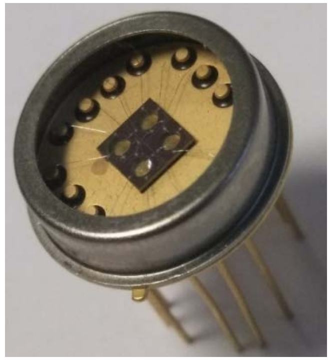






- 2 processes
- PET masks
- metallic masks





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European Regional Development Fund

Target gases

Pollutant	Maximum permitted concentration* (20 °C, 1013 mbar)		Averaging period	Maximum number of permitted excesses each year
NO_2	200 µg/m³	105 ppb	1 hour	8
	40 µg/m³	21 ppb	1 year	n/a
O_3	120 µg/m³	60 ppb	daily 8 hours mean	25 days averaged over 3 years
CO	10 mg/m³	8,6 ppm	daily 8 hours mean	n/a

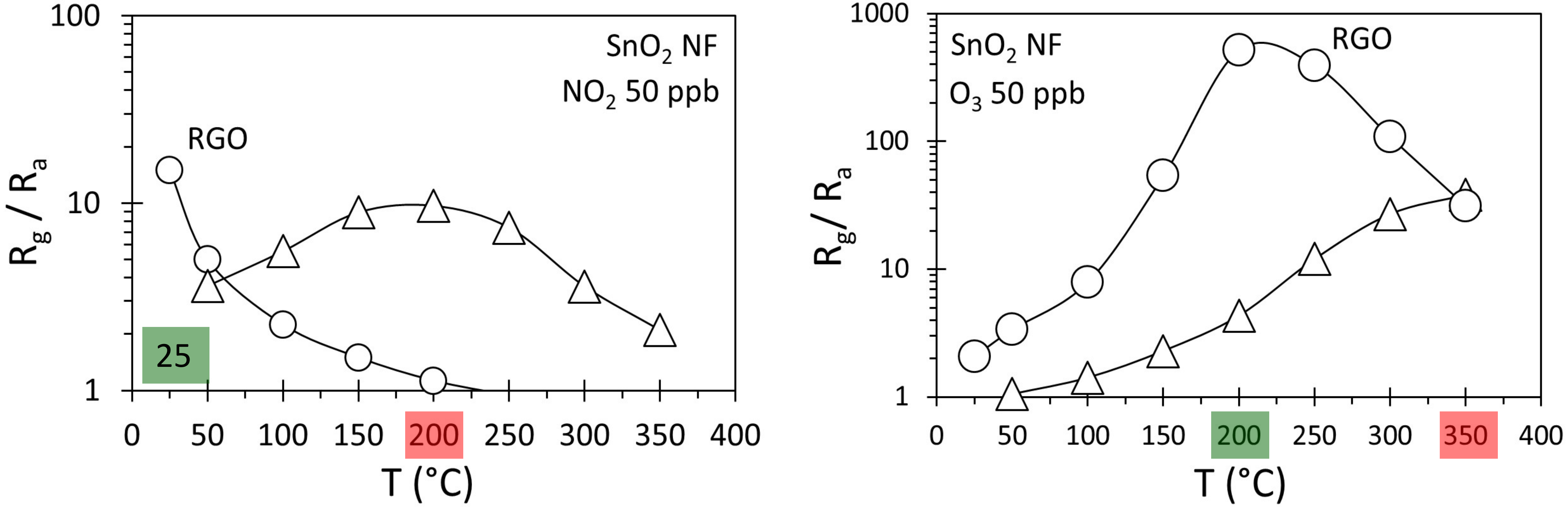
** Limit values for heath protection (Air Quality Directive EC 2008/50)*

Scenario	C_{max} (hourly average)			T (°C)	RH (%)
	NO_2 (µg/m³)	O_3 (µg/m³)	CO (mg/m³)		
Natural	15	240		min: -3 max: 45	min: 30 max: 80
Rural	50	200			
Urban	160	220			

Levels of target pollutants and **meteorological data** at the locations chosen for field campaigns provided by **regional and local AQ networks**: Extremadura, Castilla y León, Barcelona, Portugal

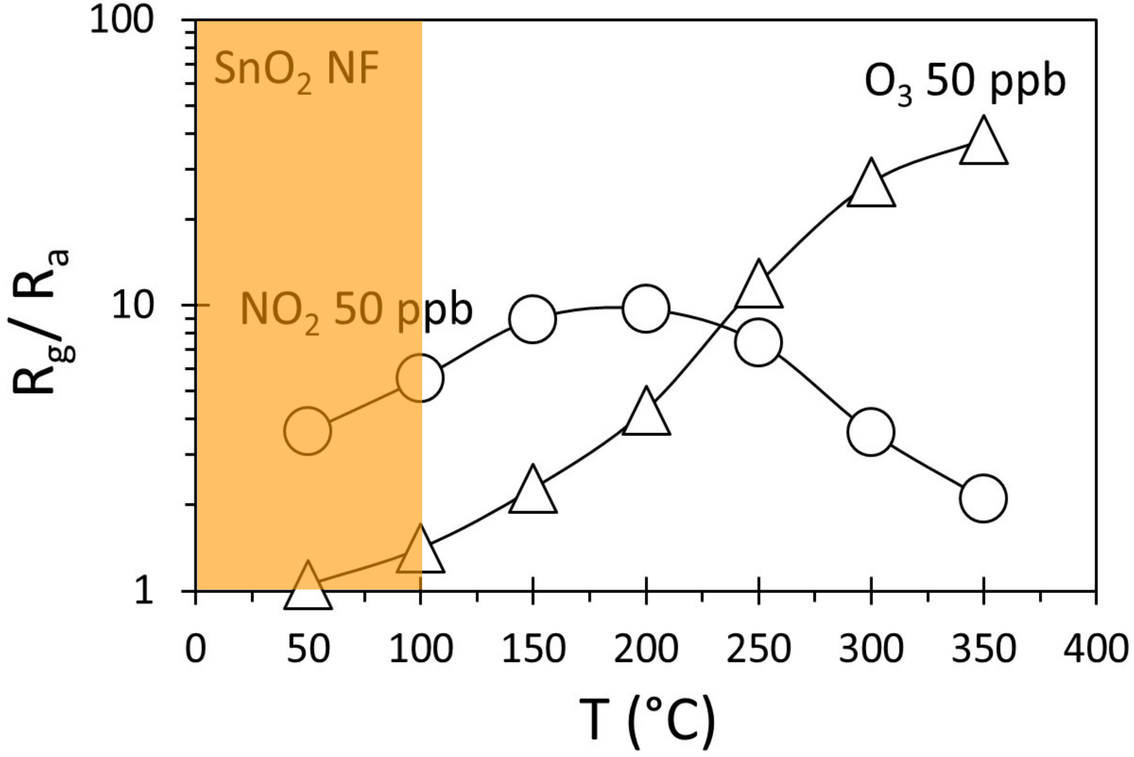
SnO_2 NF — Sensitivity

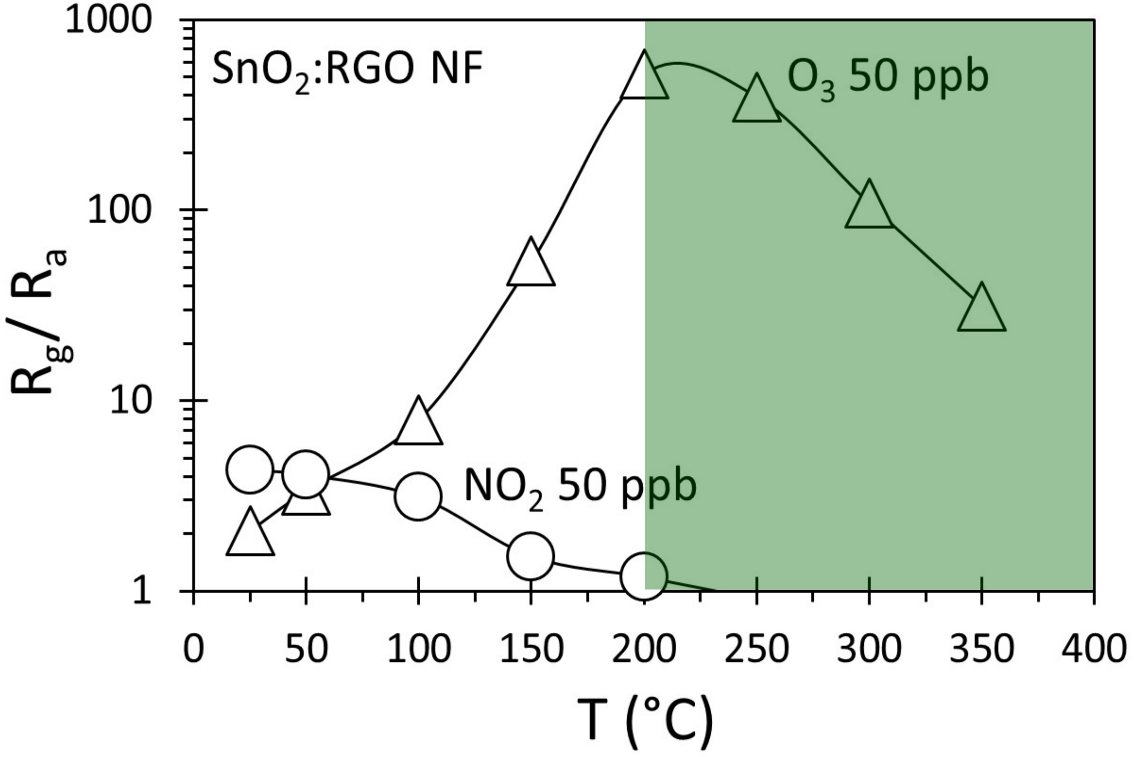
Optimal working temperature



- Higher response, higher optimal working temperature for O_3
- SnO_2 NF loaded with rGO E800: Higher low-temperature response, lower optimal working temperature for NO_2 and O_3
- No sensitive to CO (10 ppm)

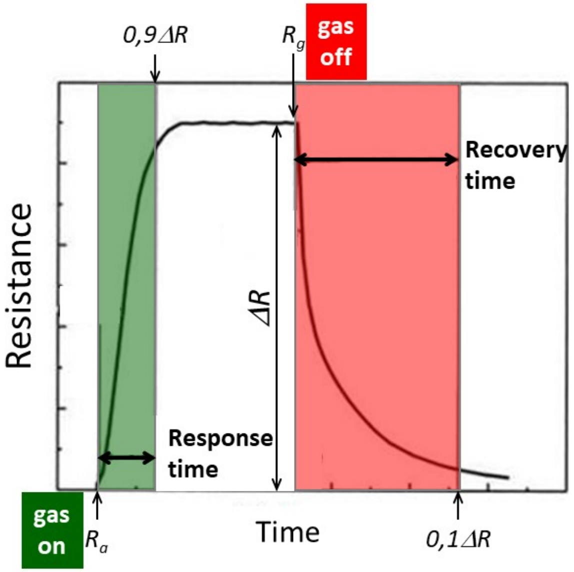
SnO_2 NF — Selectivity

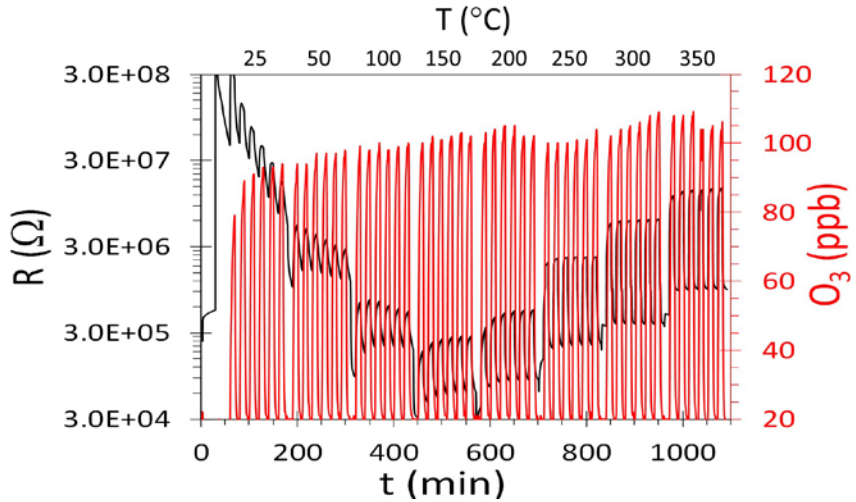


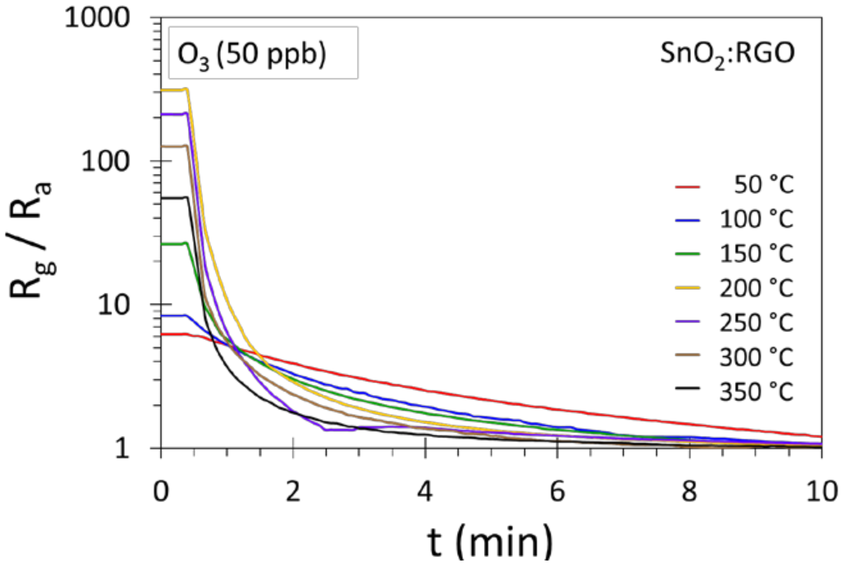


- SnO_2 NF loaded with rGO E800 @ T > 250°C for optimal selective detection of O_3
- SnO_2 NF @ T < 100°C for detecting NO_2 with cross-interference of O_3

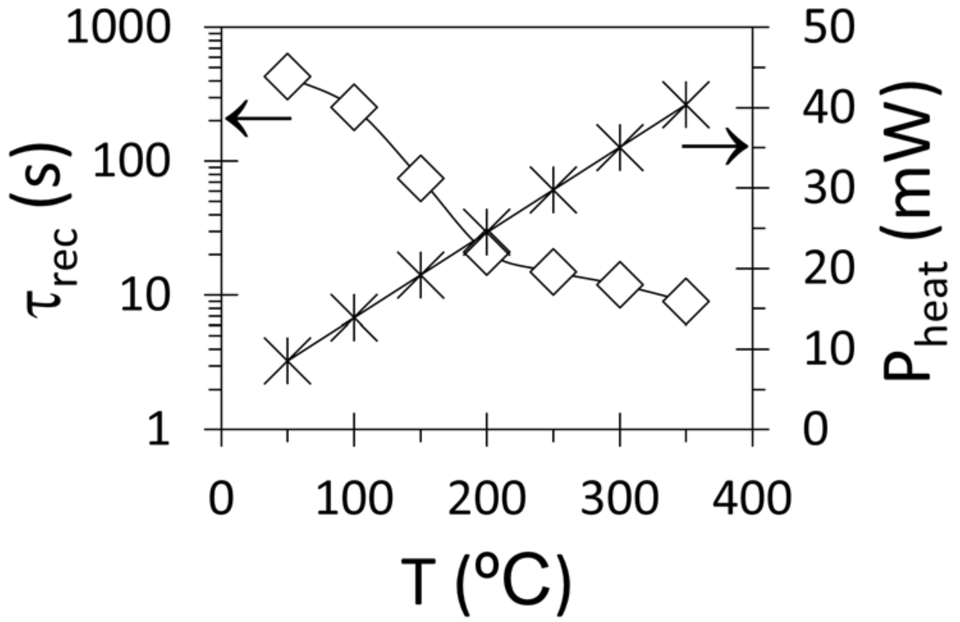
SnO_2 NF — Recovery speed







Isothermal mode $T_{ads} = T_{des}$



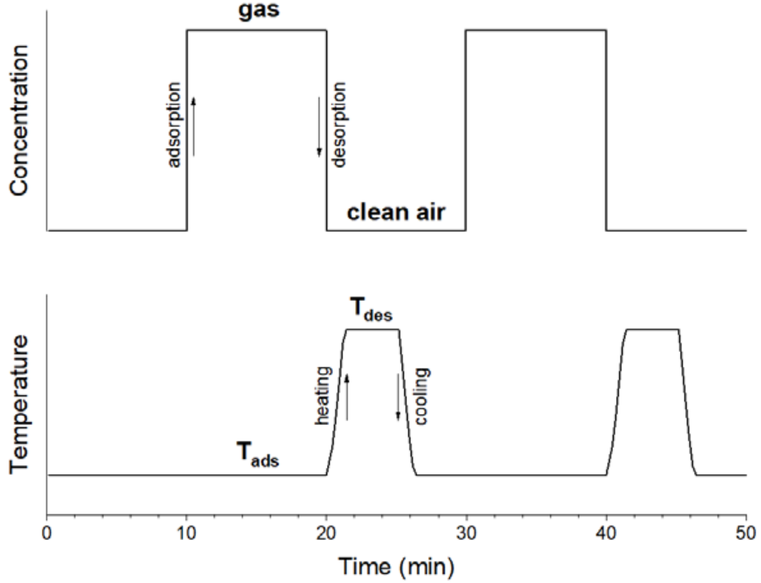
$T_{des} > 200\ ^oC$ ($P_{heat} > 25$ mW)

↓

$\tau_{rec} < 30$ s

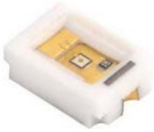
SnO_2 NF Thermal- vs. Photo-activation

Variable temperature mode
$T_{ads} < T_{des}$



Isothermal mode
Desorption under UV irradiation

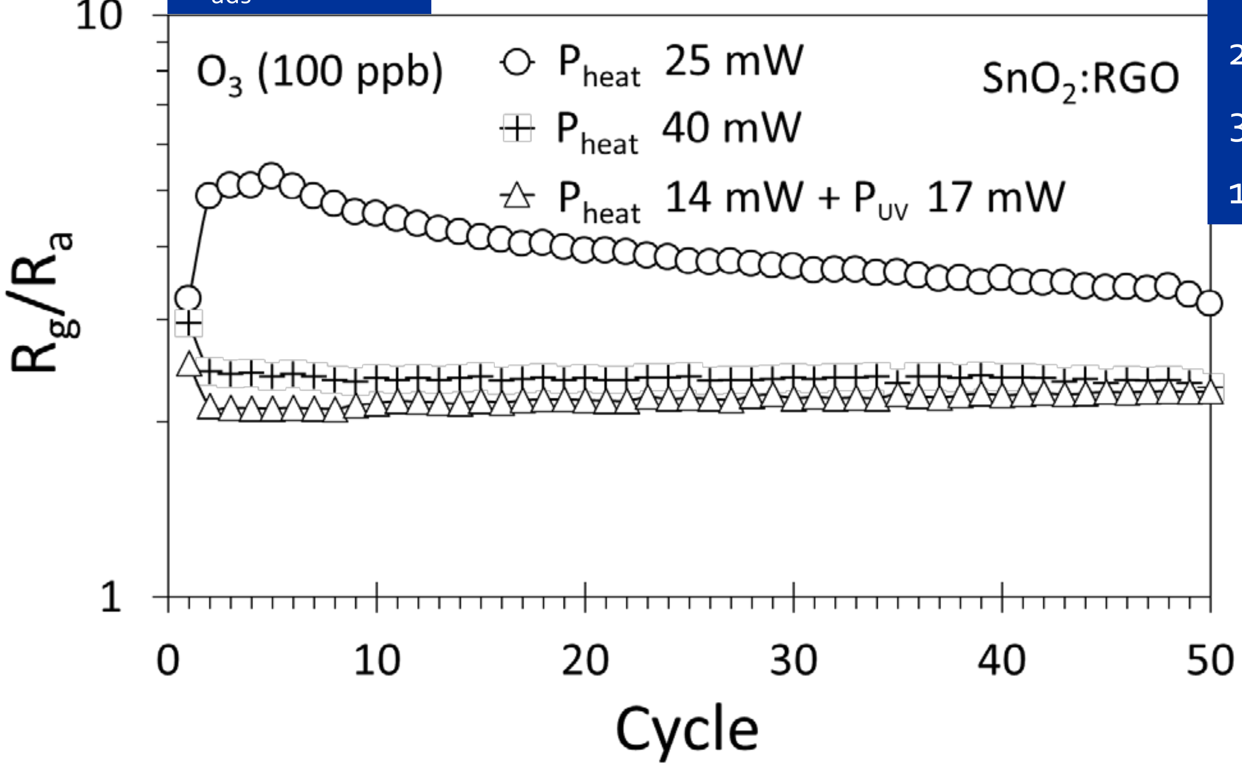
osa opto light
OCU-400 UB355



LED-UV
λ_{peak} 355 nm

T_{ads} = 100 ^oC

T_{des}
200 ^oC
350 ^oC
100 ^oC



- Photoactivation is suitable for rapid gas desorption at low temperature
- Less energy consumption, no thermal or mechanical stresses on microhotplate

SnO_2 NF CO

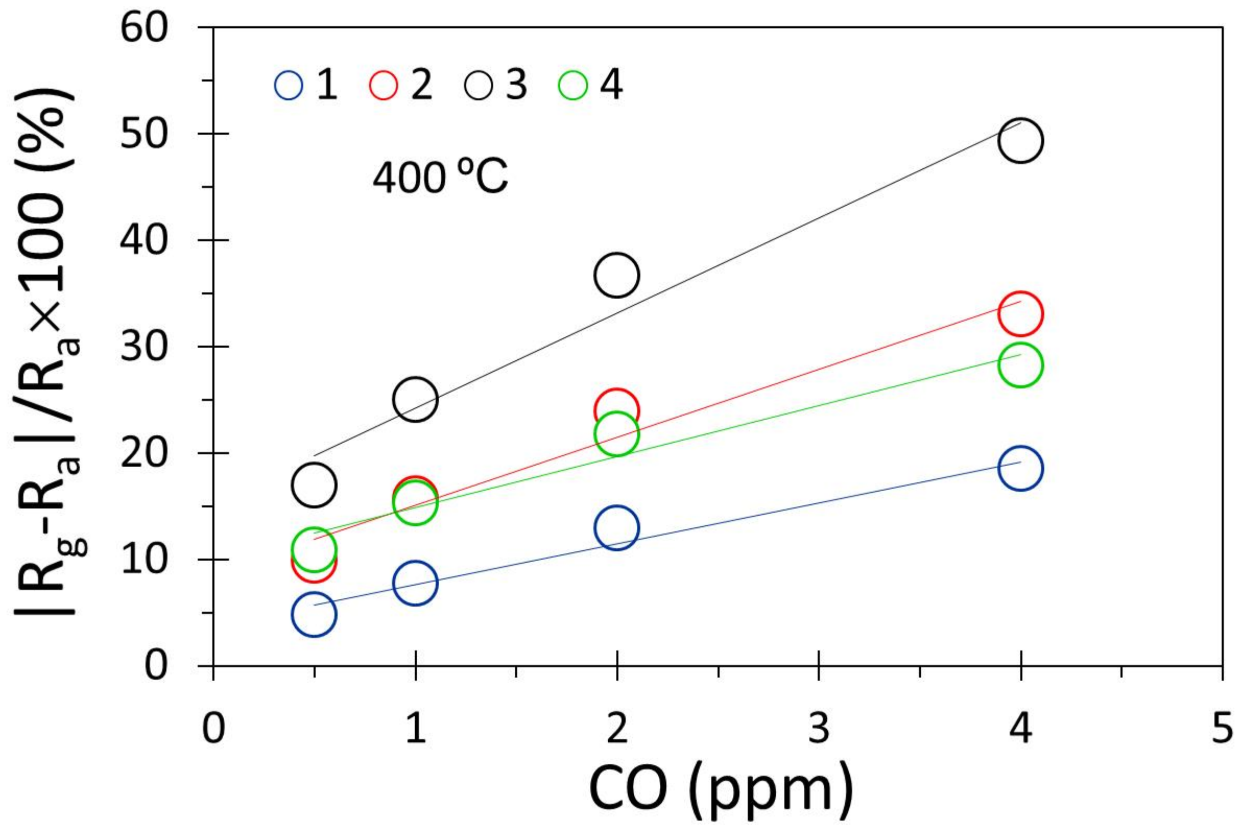
SIGMA-ALDRICH

US Research Nanomaterials

#	Dopant	$X^{a)}$ %$wt^{b)}$
1	Pt NP (3 nm) Dispersion in H_2O 1 mg/mL	0.2
2	Pd NP (15 nm) Dispersion in H_2O 1 mg/mL	0.5
3	$PdCl_2$ Powder	0.3
4	Au NP (15 nm) Dispersion in H_2O 1 mg/mL	0.35
5	$AuCl_3$ Powder	0.3

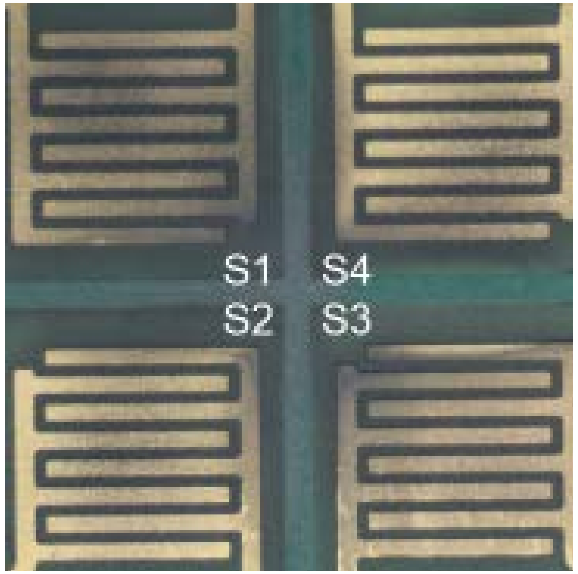
→ PdO_x

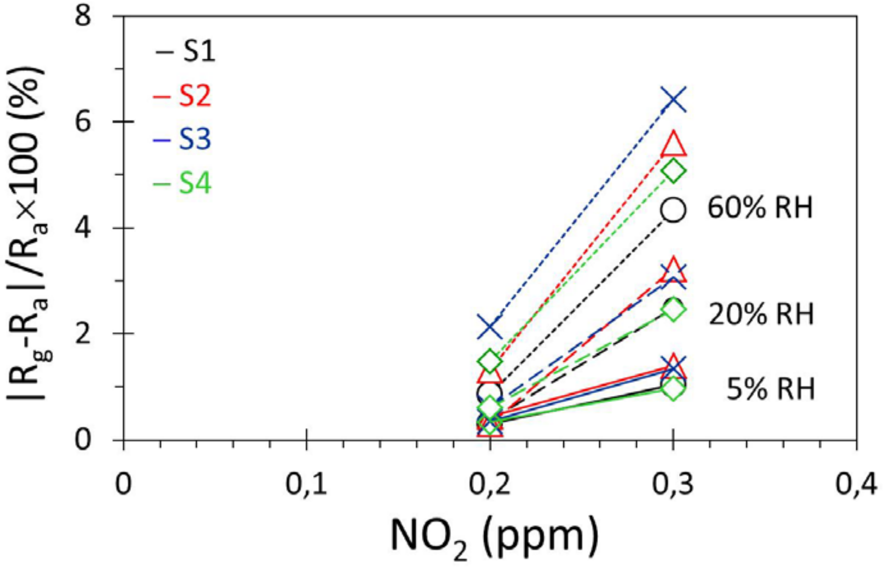
a) X = Pt, Pd, Au b) %wt = X:Sn

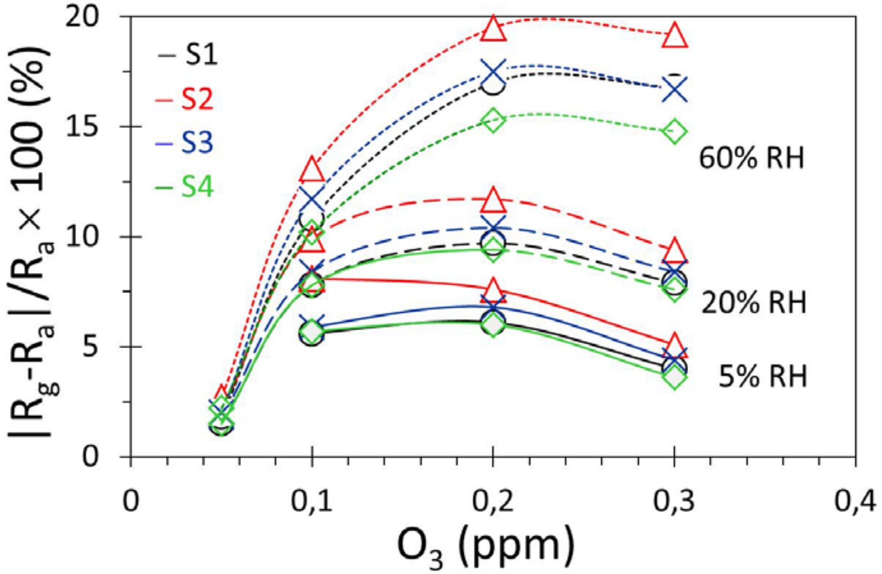


- Optimal temperature 400 ºC (P_{heat} 45 mW)
- Limit of detection CO < 0.5 ppm
- Effect of graphene needs to be investigated

Graphene rGO E800

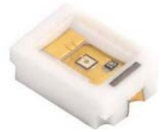






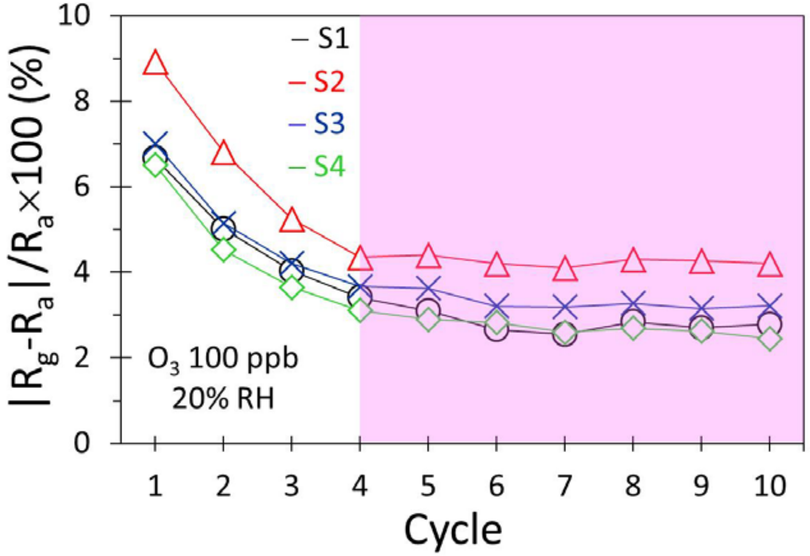
- Limit of detection NO_2 ~ 200 ppb
- Limit of detection O_3 ~ 50 ppb
- No sensitive to CO (10 ppm)
- Photoactivation speeds up gas desorption →

OCU-400 UB355



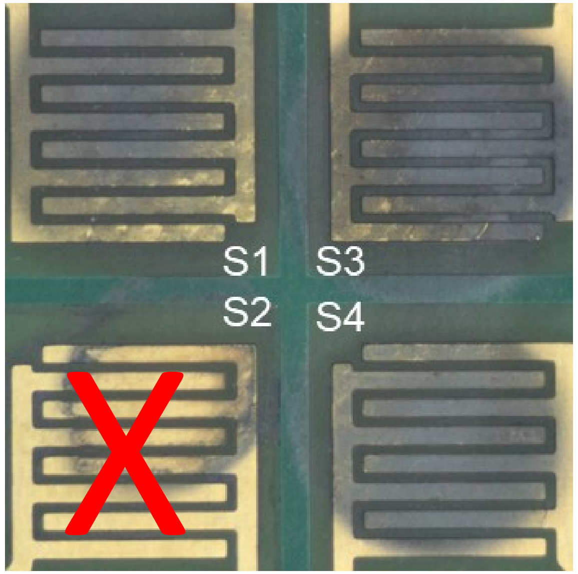
LED-UV

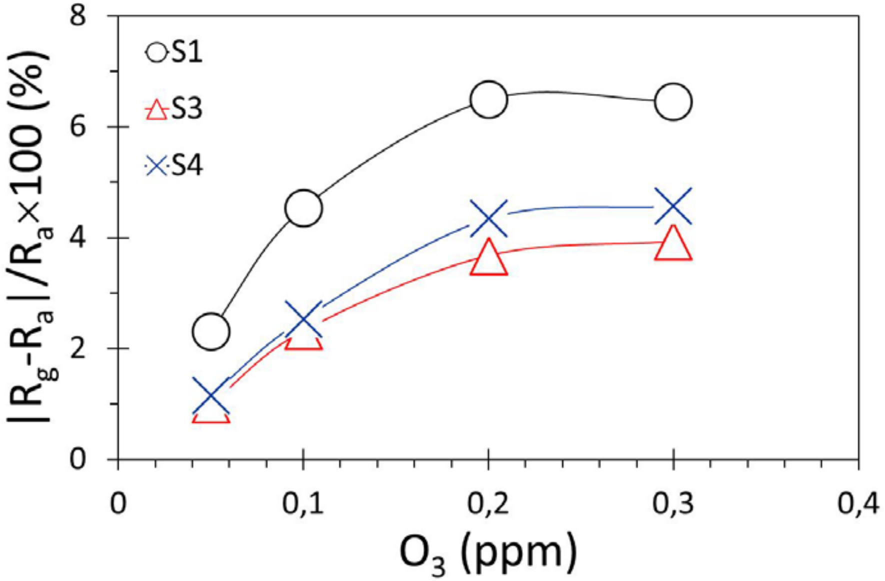
λ_{peak} 355 nm

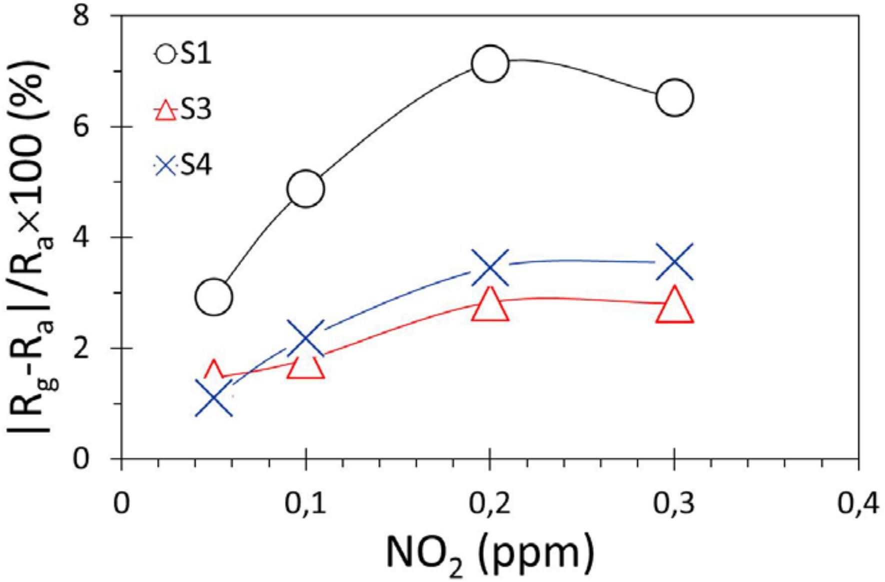


Graphene

XGnP



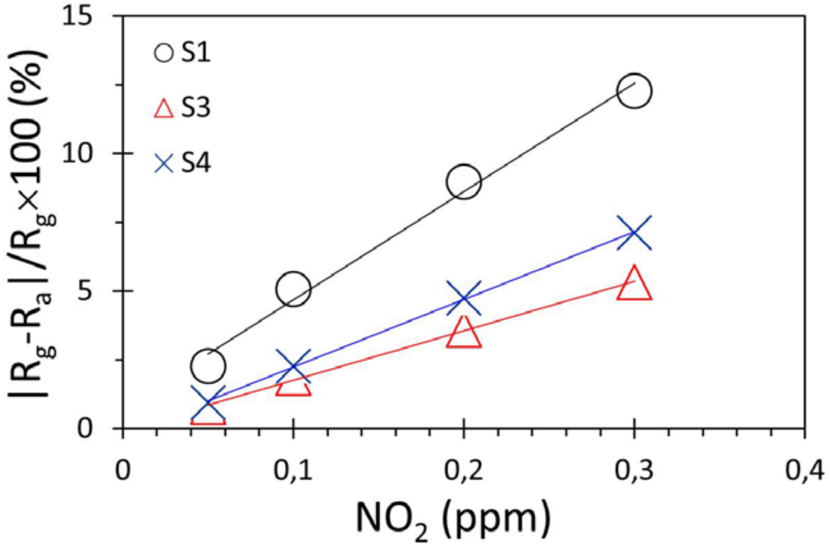




- Limit of detection NO_2 ~ 50 ppb
- Limit of detection O_3 ~ 50 ppb
- No sensitive to CO (10 ppm)
- Photoactivation speeds up gas desorption →

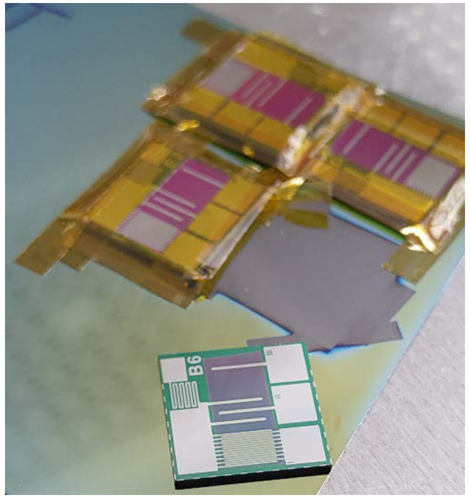
OPTAN
OPTAN® 3535

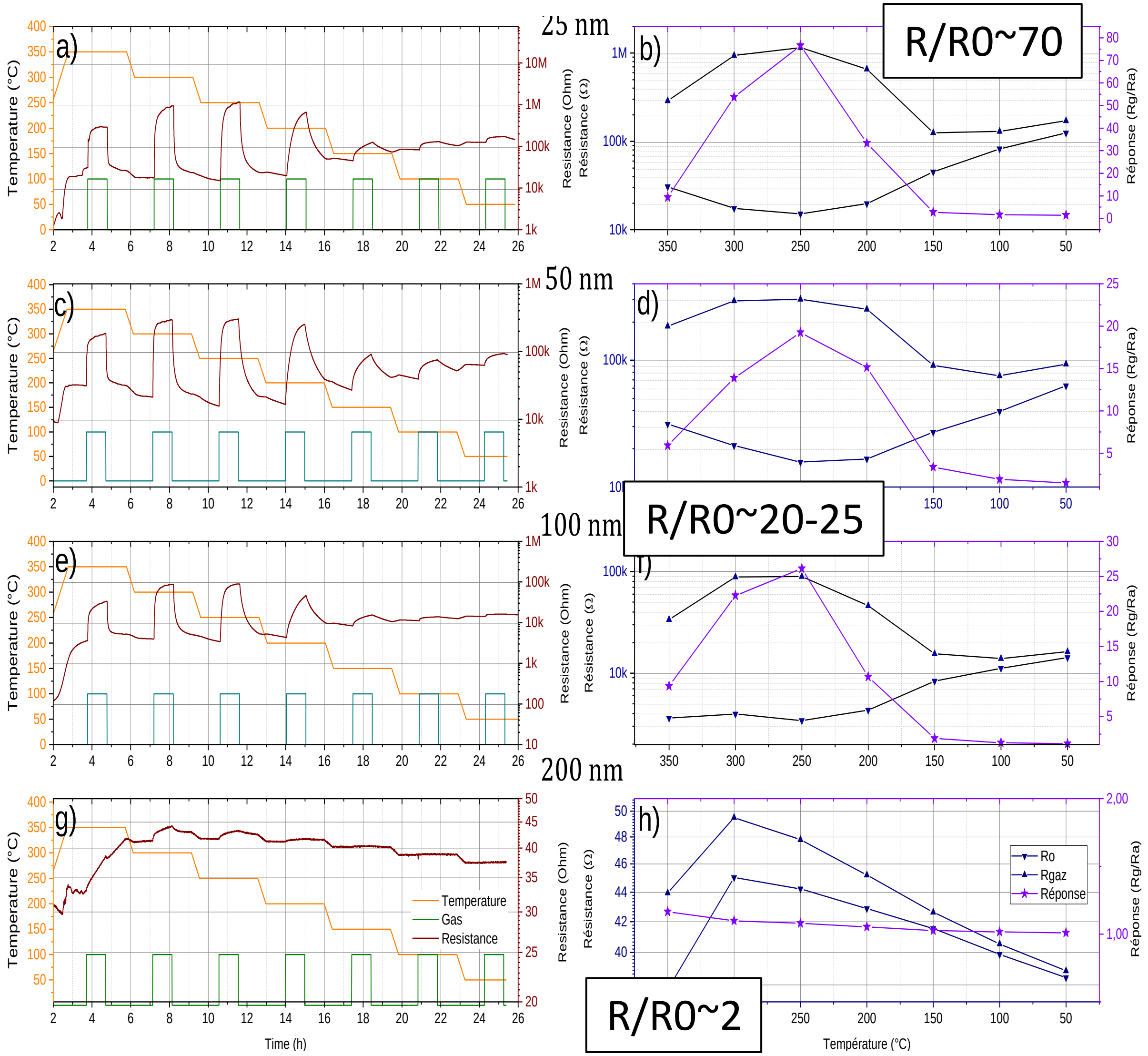
LED-UV
λ_{peak} 255 nm



ZnO:Ga Response

1 Simplified devices





- Thicknesses from 25 to 230 nm measured
- Simplified device in specific test chamber
- Thinnest film are more sensitive (at ~ 250 °C)
- 25 and 60 nm thick layers have been studied on microsensors

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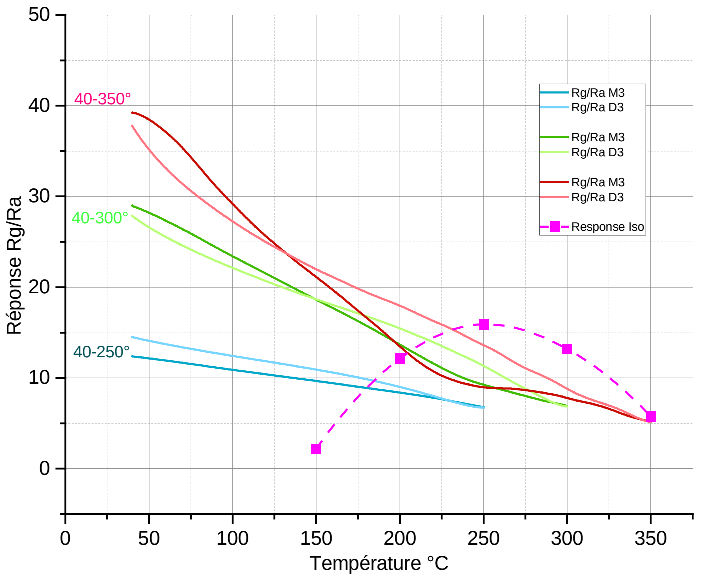
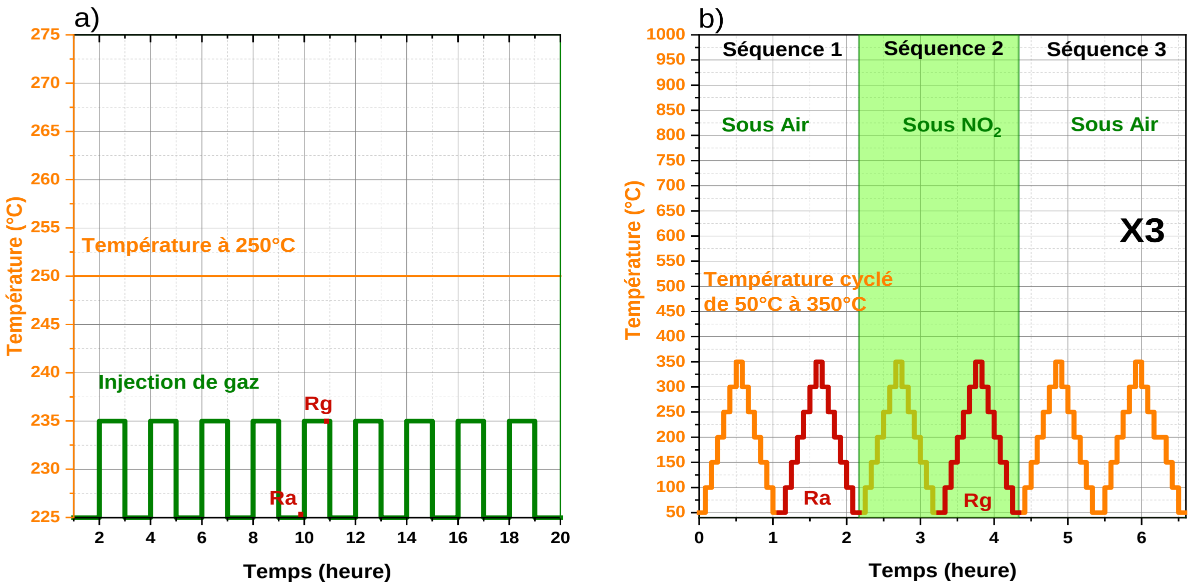
Nan Sen-AQM

ZnO:Ga Response

2 Measurement modes



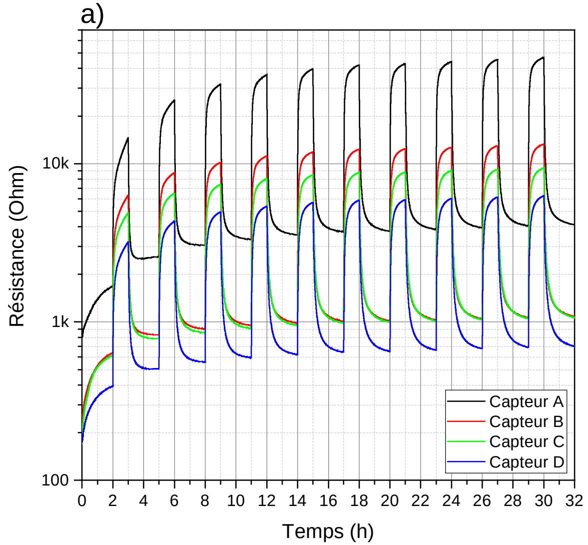


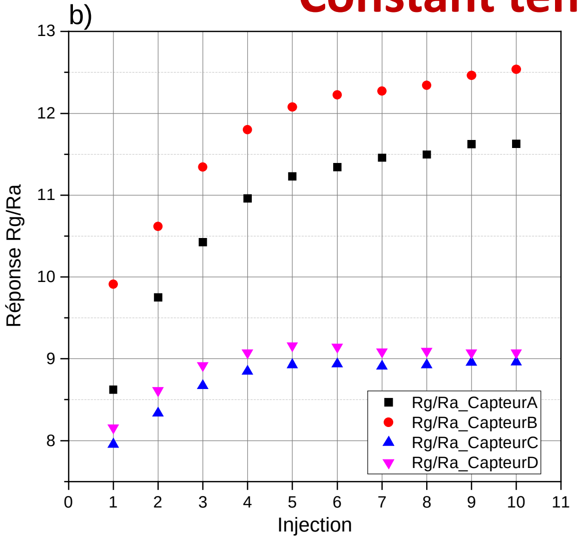
- 2 types of measurement mode:
- Classical constant temperature mode (250 °C)
- Cycled temperature mode (50-350 °C -> reduced to 50-250 °C to avoid ageing)

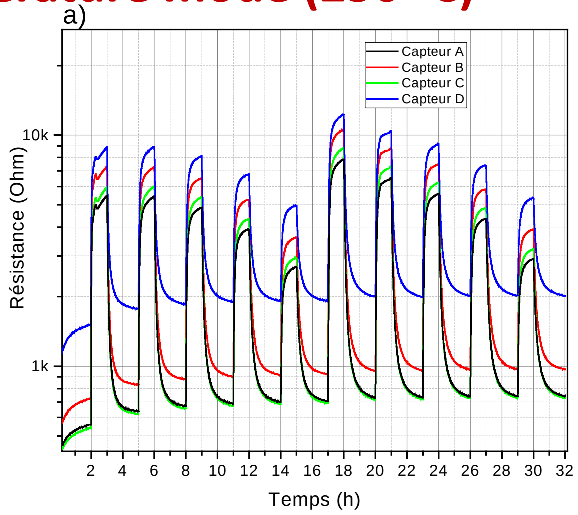
ZnO:Ga Response

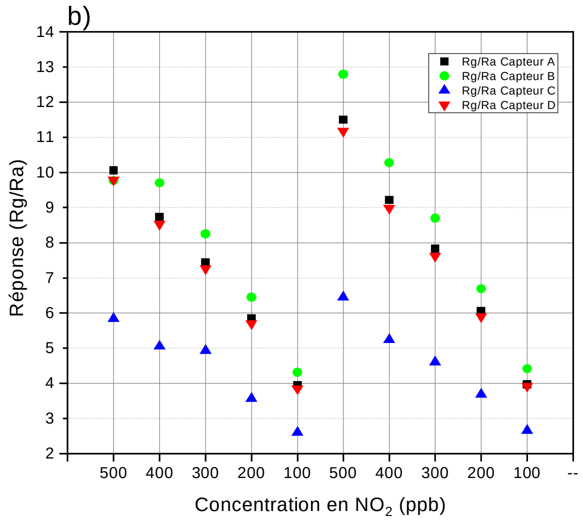
3 Responses Rgaz/Rair

Constant temperature mode (250 °C)

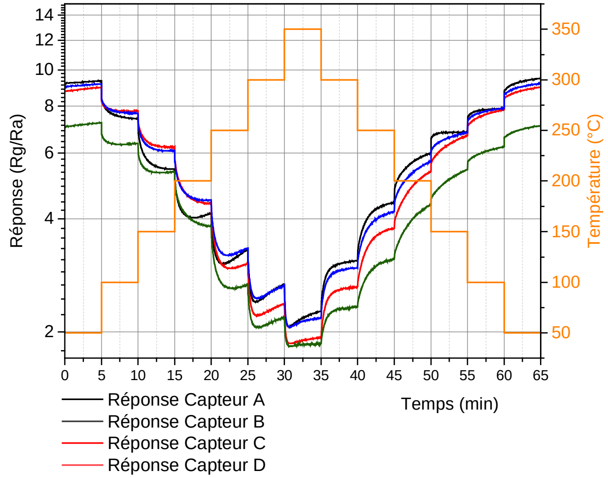








Cycled temperature mode



- Stabilization of the results in constant mode (some disparity between 4 sensors)
- Sensitivity to NO_2 variable concentration (measured under 50% RH)
- Cycled temperature mode seems efficient

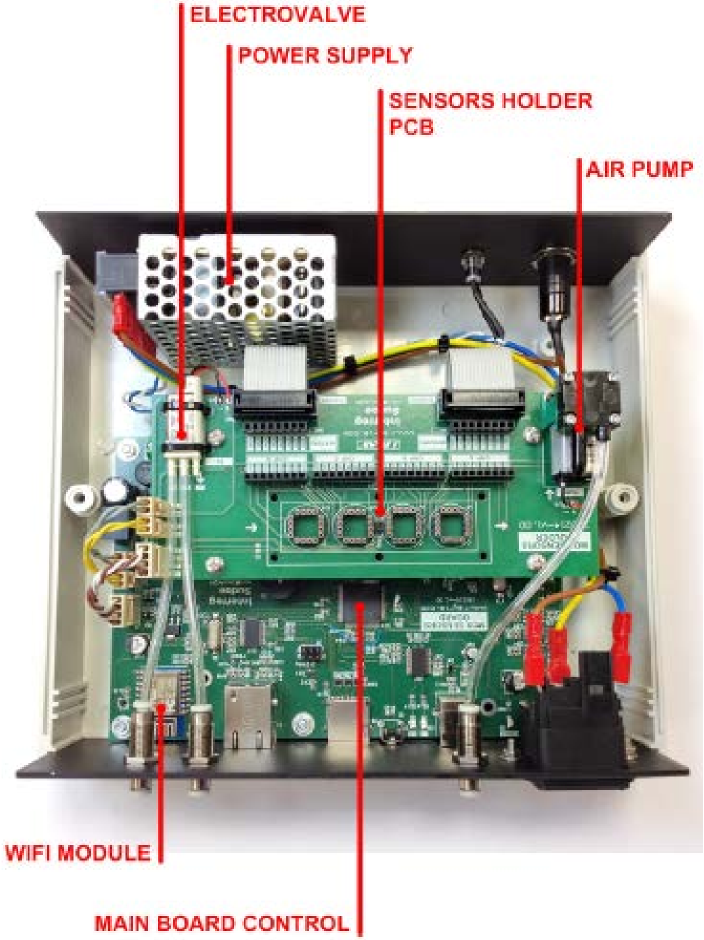
Interreg Sudoe
EUROPEAN UNION
NanoSen-AQM
European Regional Development Fund

Summary

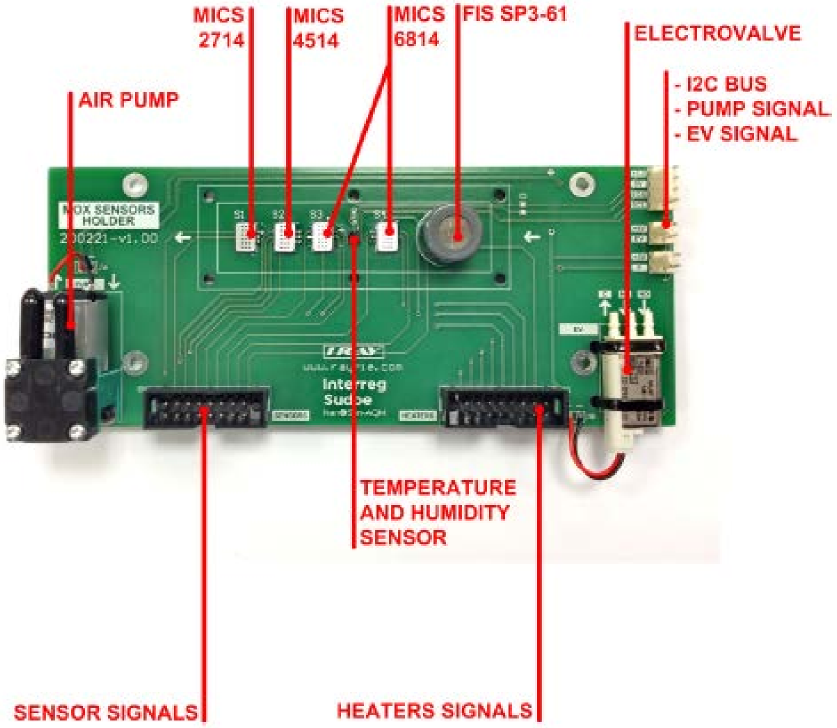
	Advantage	Disadvantage
Thin films and nanofibers oxides	NO_2, O_3 and CO could be detected at low or moderate temperature	Cross-sensitivity
Graphene sensitive layer	Room temperature detection	Cross-sensitivity
UV irradiation	Improve sensing performance (response, recovery time, linearity, stability)	
Electrohydrodynamic printing (CSIC)	Cost-effective technique, simple operating conditions (ambient T and P), and high versatility and flexibility of the proscess (broad diversity of solutions and dispersions)	
Sputtering technique (CIRIMAT)	Fully compatible with MEMS technology	
Microhotplate based on MEMS technology (LAAS)	Efficient, wide temperature range with low consumption, homogeneous heating, shadow mask usable, constant and cycled temperature modes available	

P2.1 delivery

MOX Module

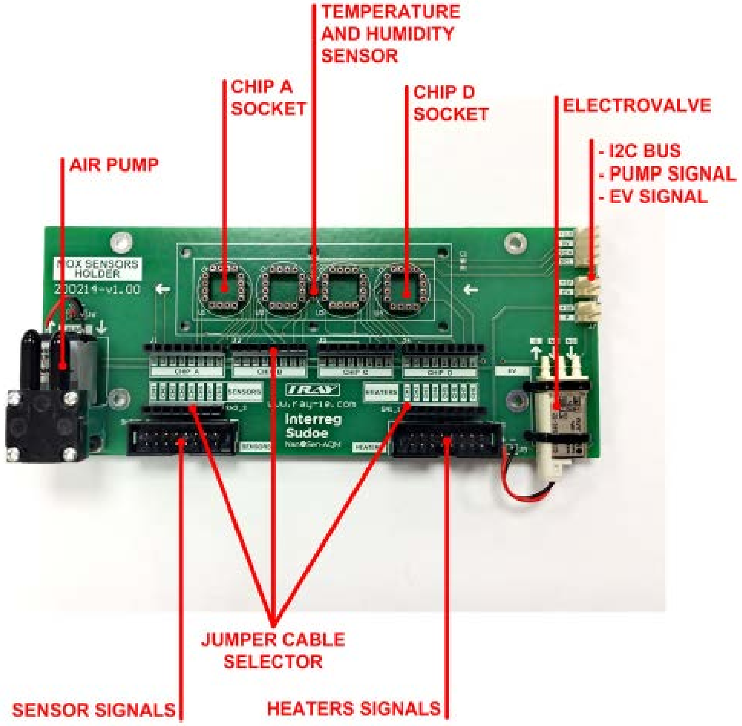


Switchable sensor board



Commercial sensors

FMXCO



Nanosensors

CNRS (FMXCN)

CSIC (FMXCS)

P2.1 delivery

FMXCO

Commercial sensors

NO_2 (4) O_3 (1) CO (3)

Sensor heaters

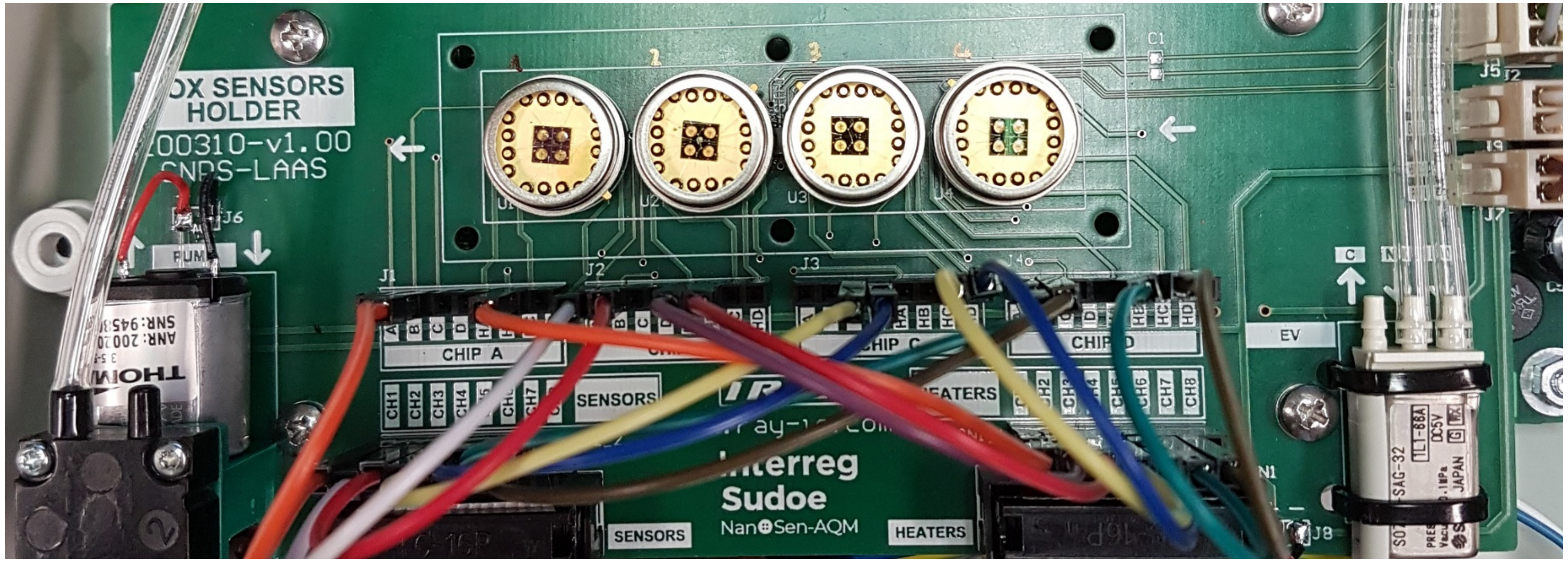
CH	SENSOR	DET. GAS	Range (pbb)	R_0 range (Kohm)	R_0 nom (Kohm)	R_s det. range (Kohm)	V_h (V)	I_h (A)	R_h (Ohm)	P_h (mW)
1	MiCS 2714 (OX)	NO2	50 - 10000	0.8 - 20	10	3 - 800	1,7	0,026	66	43
2	MiCS 4514 (OX)	NO2	50 - 10000	0.8 - 20	10	3 - 800	1,7	0,026	66	43
3	MiCS 4514 (RED)	CO	1000 - 1000000	100 - 1500	1000	3200 - 10	2,4	0,032	74	76
4	MiCS 6814 (OX)	NO2	50 - 10000	0.8 - 20	10	3 - 800	1,7	0,026	66	43
5	MiCS 6814 (RED)	CO	1000 - 1000000	100 - 1500	1000	3200 - 10	2,4	0,032	74	76
6	MiCS 6814 (OX)	NO2	50 - 10000	0.8 - 20	10	3 - 800	1,7	0,026	66	43
7	MiCS 6814 (RED)	CO	1000 - 1000000	100 - 1500	1000	3200 - 10	2,4	0,032	74	76
8	FIS SP3-61	O3	20 - 1000	3 - 100	50	175 - 10000	5,0	0,080	41	400

- Gas concentration range of interest at the lower limit of detection range
- Isothermal mode: $P_{CO} > P_{NO2}$, PO_3 >>

P2.1 delivery

FMXCN

Nanosensors CNRS (ZnO:Ga thin films)



Platform	1		2		3		4	
Channel	Ch1	Ch2	Ch3	Ch4	Ch5	Ch6	Ch7	Ch8
Film thickness (nm)	25	25	25	25	50	50	50	50
Temperature	Constant	Cycled	Constant	Cycled	Constant	Cycled	Constant	Cycled
Power (mW)	20	20-30	25	5-25	25	5-25	25	5-25

P2.1 delivery

FMXCS

Nanosensors CSIC (SnO_2 NF layers)

Platform	1		2		3		4	
Channel	Ch1	Ch2	Ch3	Ch4	Ch5	Ch6	Ch7	Ch8
Sensing material	SnO_2:RGO	SnO_2:RGO	SnO_2:PRG	SnO_2:PRG	SnO_2:GNPL	SnO_2:GNPL	SnO_2:Pt NP	SnO_2:Pt NP
Power (mW)	41	41	14.5	41	14.5	41	14.5	14.5