Design Elements and Prototypes of Metal Oxide Based Gas Sensors

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Master degree

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Parterships

- LEOS, Lab of Electrochemistry and Organic Syntheses, Dept. of Basic and Applied Sciences for Engineering, Sapienza University of Rome

- IMM Institute of Microelectronics and Microsystems of National Research Council of Rome Tor Vergata

- MNF, Micro-Nano characterization and fabrication Facility of Fondazione Bruno Kessler in Trento

Introduction

- **Microelectronics: Chemoresistive Gas Sensors**

- **Heterostructures:**
  - SnO_2 99 wt% /rGO 1 wt% (SG)
  - Polyaniline Emeraldine Salt (PANI ES) 90 wt% /SnO_2 9.9 wt% /rGO 0.1 wt% (SGP)

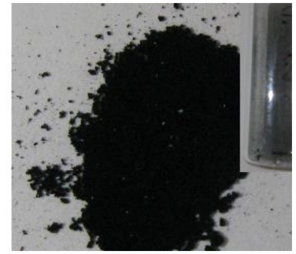
- **Methods:**
  - Hydrothermal Synthesis (SG)
  - In situ Polymerization (PANI ES on SG)
  - Characterizations (XPS, XRD, SEM)
  - Functional Characterization
  - Target: CO, NO_2

- Navazani, S.; Shokuhfar, A.; Hassanisadi, M.; Di Carlo, A.; Shahcheraghi, N. Fabrication and Characterization of a Sensitive, Room Temperature Methane Sensor Based on SnO2@reduced Graphene Oxide-Polyaniline Ternary Nanohybrid. Materials Science in Semiconductor Processing 2018, 88, 139–147. https://doi.org/10.1016/j.mssp.2018.08.006.

Syntheses Materials and Methods

SG

SnO_2 /rGO Hydro-thermal synthesis



SGP

SnO_2/rGO/PANI Chemical polymerization.

- GO(1 wt%) in 40 mL of tin (IV) chloride pentahydrate solution (0.5 mol L^{-1})
- sonicated for 60 min
- heated 180 ° C for 4 h
- allowed to cool at room temperature
- washed several times with deionized water and ethanol
- dried at 60 ° C under vacuum.

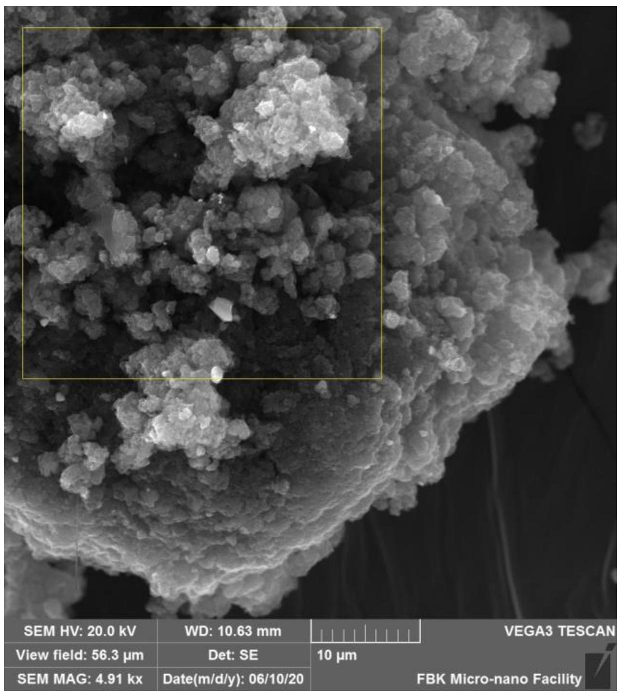
- Aniline (0.1 mL) and SnO_2/rGO (10 mg) were added under stirring, to 40 mL HCl 1M solution.
- put into an ice-water bath and stirred one hour.
- 5 mL of a 0.2 M ammonium persulfate-HCl solution were added dropwise to the cold mixture.
- under stirring for 16 h at room temperature
- dark green solution was obtained
- solution was then filtered and rinsed
- dried under vacuum at 60 ° C for 12 h.

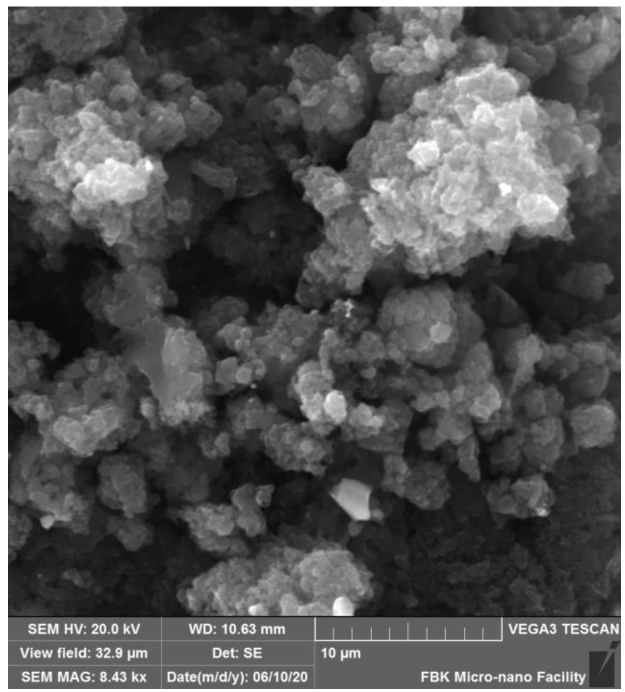
L. Li, S. He, M. Liu, C. Zhang, W. Chen, *Anal. Chem.* **87**, 1638–1645 (2015).
S. Navazani, A. Shokuhfar, M. Hassanisadi, A. Di Carlo, N. Shahcheraghi, *Materials Science in Semiconductor Processing* **88**, 139–147 (2018).

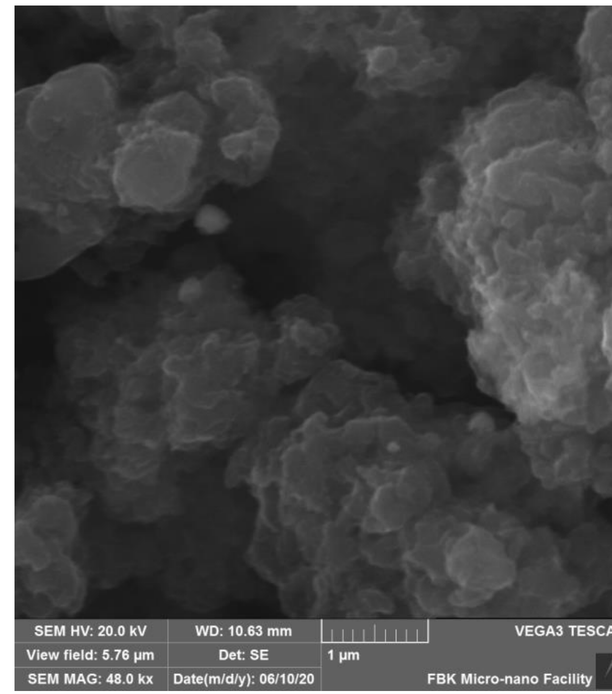
SGP SEM Imaging

Imaging SE collection: morphological and topographical informations

- PANI in SGP porous structure conformation
- Polarization effect occurs during the imaging acquisition





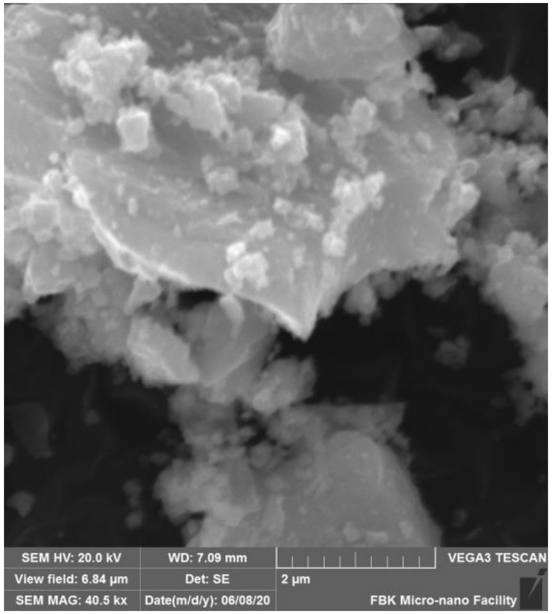


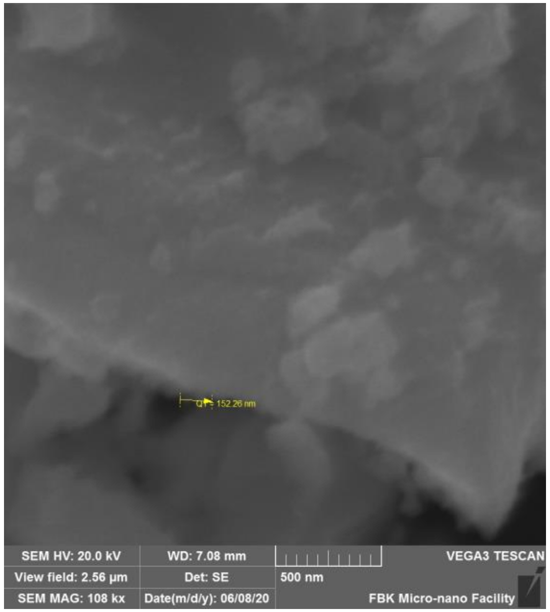
Scanning Electron Microscope images are realized with VEGA3 TESCAN Everhart-Thornley (ET) SE relevator MNF FBK Trento 06/08/20.

SG SEM Imaging

Imaging SE collection: morphological and topographical informations

- Flake of rGO rises in SG
- Image is graphically elaborated to evaluate the clusters dimensions (80 nm)

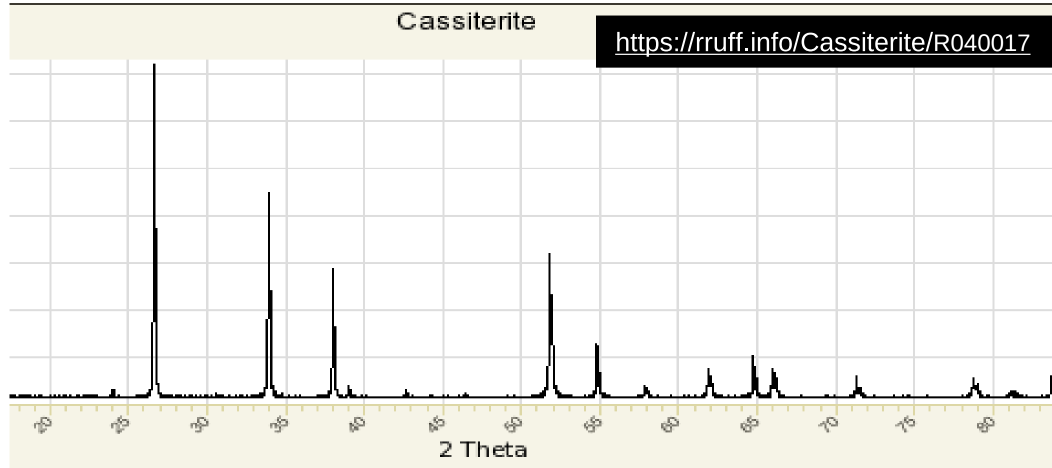


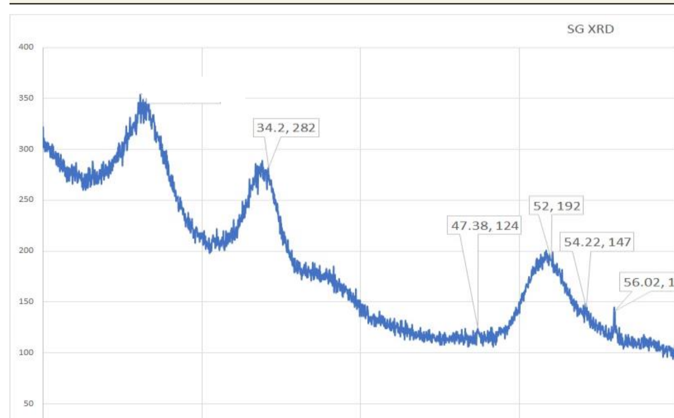


Scanning Electron Microscope images are realized with VEGA3 TESCAN Everhart-Thornley (ET) SE relevator MNF FBK Trento 06/08/20c

SG XRD Analysis

- Average crystallite dimensions
- 3.1± 0.4 nm (Scherrer)
- 2.6± 1.1 nm (WH)
- Peaks: 26.4 (110), 33.8 (101), 51.5 (211).
  Cassiterite white mineral
- SnO_2
- Broadening Effect

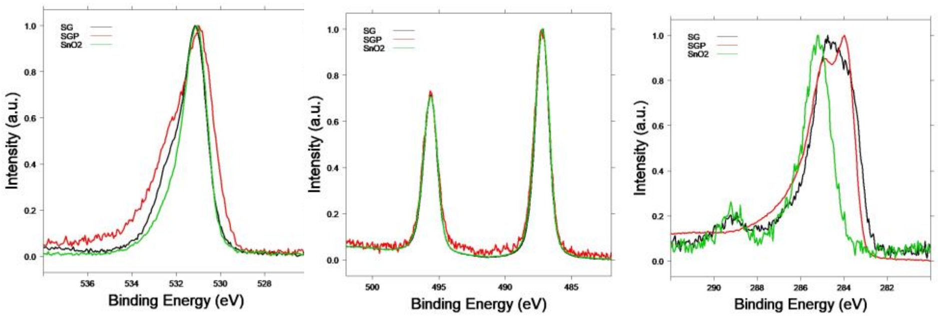




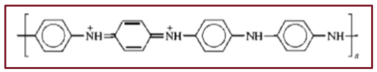
Brag Brentano (Theta/2Theta) - scan 20 – 60, step 0,02, time step 10 sec.

SG & SGP XPS Analysis

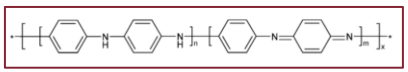
Core electrons O 1s, Sn 3d e C 1s

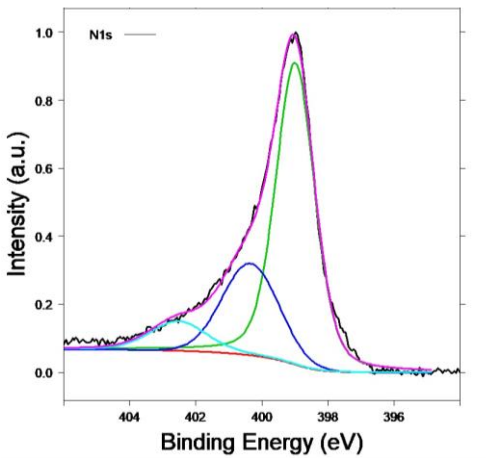


PANI-ES



PANI





Fitting of core electron spectra of N1s

- Stoichiometric ratio of core electrons

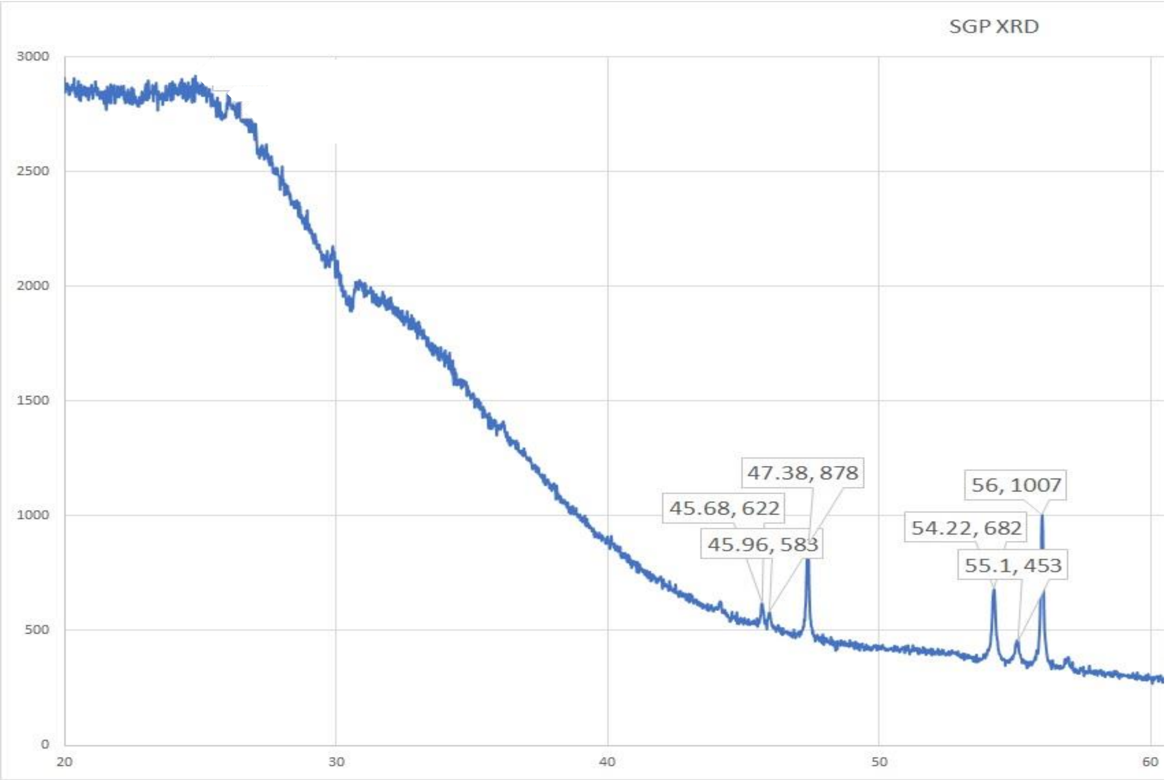
Sample	O %	Sn %	C %	Sn/O	N %	S %
SGP	8.2	0.6	77.6	0.07	12.3	1.4
SG	55.9	27.6	16.2	0.49	-	-

- Majority of C sp^2 with respect to C sp^3

- Nitrogen fitting peak

- 1s core spectra is fitting in its coordinated form: (-N= a 399.3) prevails over other peaks, N^+ (>400 eV) (-N- a 398.2)

SGP XRD Analysis

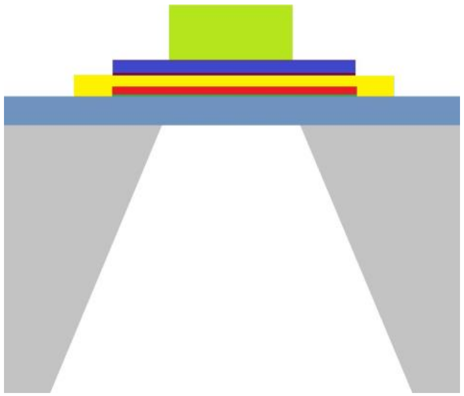


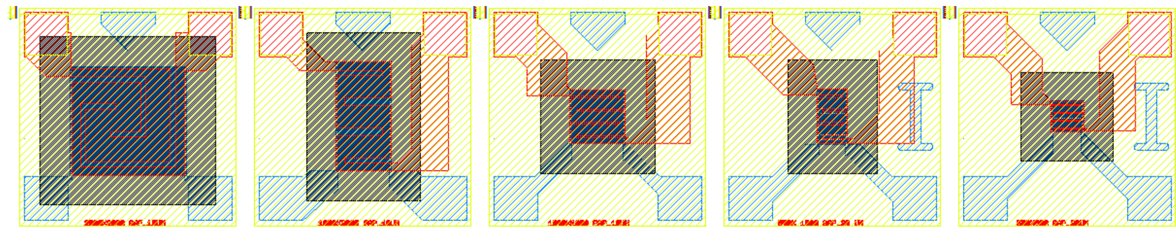
Brag Brentano (Theta/2Theta) - scan 20 – 60, step 0,02, time step 10 sec.

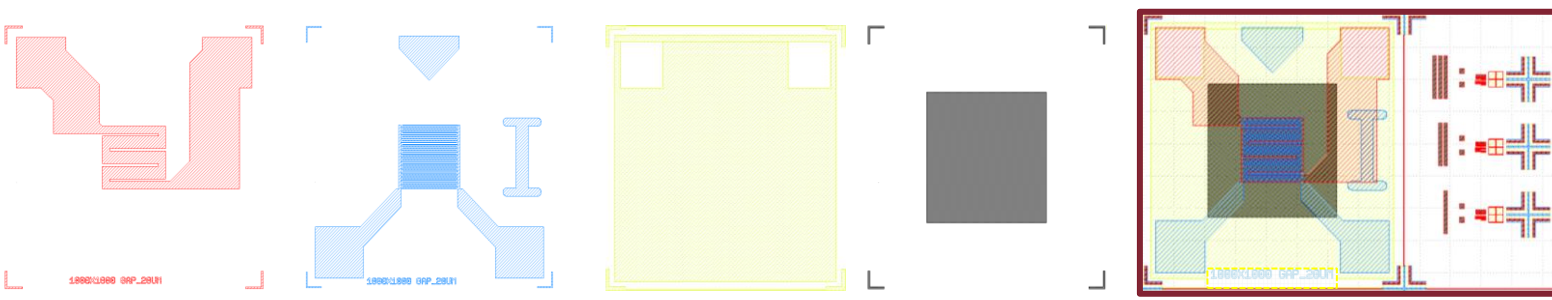
- PANI peaks are 25.1 (200), 20.9 (020) and 15.2 (011) a big signal at low angles indicates an amorphous structure

* Navazani, S.; Shokuhfar, A.; Hassanisadi, M.; Di Carlo, A.; Shahcheraghi, N. Fabrication and Characterization of a Sensitive, Room Temperature Methane Sensor Based on SnO2@reduced Graphene Oxide-Polyaniline Ternary Nanohybrid. Materials Science in Semiconductor Processing 2018, 88, 139–147. https://doi.org/10.1016/j.mssp.2018.08.006.

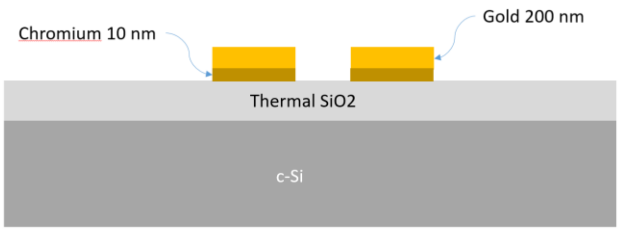
Lithography







Gold-Silicon Process Flow

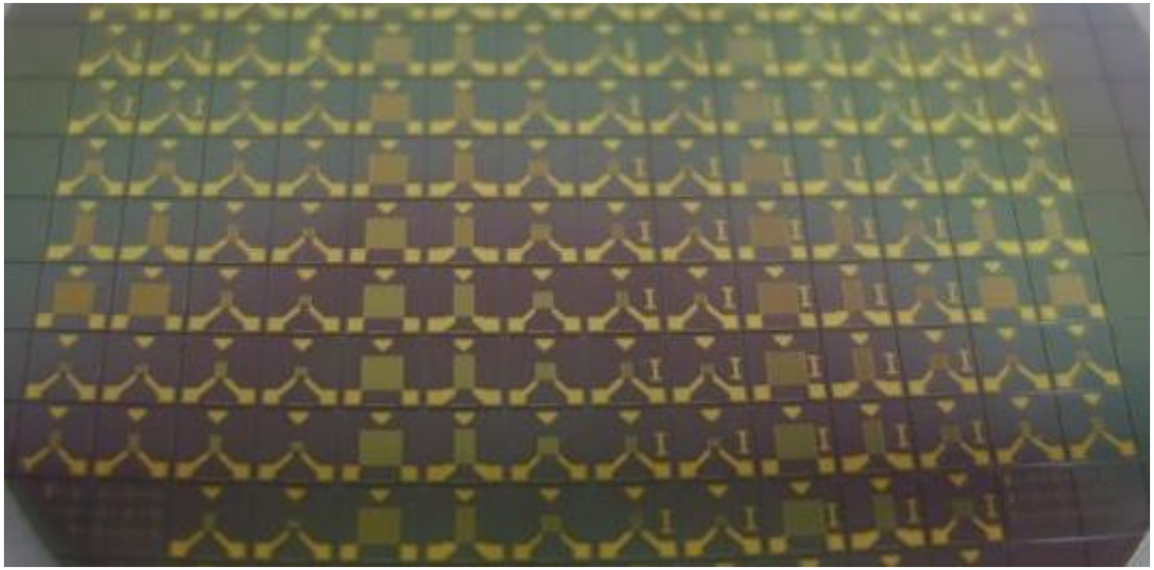


- SUBSTRATE: 3 INCHES **WAFER SI(100)**
- CLEANING IN **HF DILUTED 1:20**
- **PVD E-BEAM** 10NM CR +

THERMAL EVAPORATION OF 200 NM AU

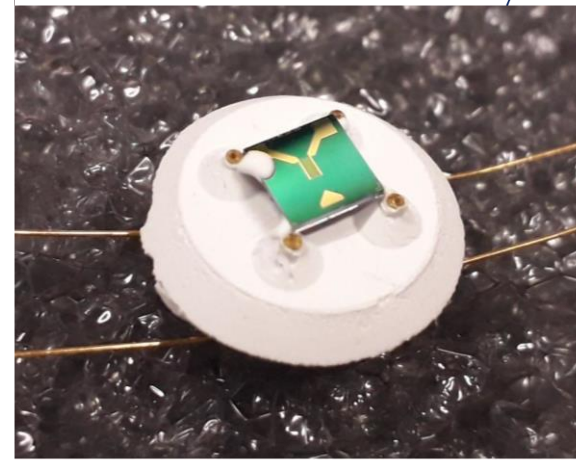
- CR DEPOSITION RATE 5 Å/S
- AU DEPOSITION RATE 10 Å/S

- **HMDS** IN VACUUM FOLLOWED BY SPIN-COATING OF PHOTORESIST **S1813** (4000 RPM T= 60 S)
- **SOFT BAKING:** HOT PLATE T=115 ° C, T=1 MIN
- POWER UV-LIGHT **11.3 mW/cm^2**
- PHOTORESIST **DEVELOP** MF319 T= 2’ 10’’
- **R**EACTIVE **I**ON **E**TCHING IN **O**XYGEN AT POWER 70 WATT, T=1 MIN
- **ETCHING AU**: 200NM, 54 S
- **ETCHING CR** 10 S, ETCH RATE: 1.47 NM/S
- **REMOVAL** OF PHOTORESIST IN ACETONE AND ULTRASOUND T=3 MIN/ EVENTUALLY OXYGEN RIE



Gold-Silicon Wafer after cutting step

IMM Institute for Microelectronics and Microsystems

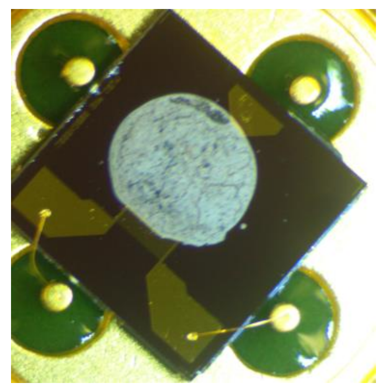


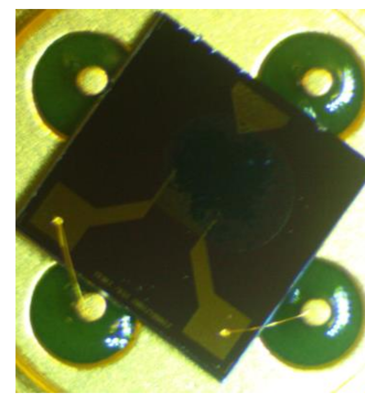
Alumina Packaging solution

PACKAGING SOLUTION: AFTER CLEANING WAFER IS DICED, AND PACKAGE

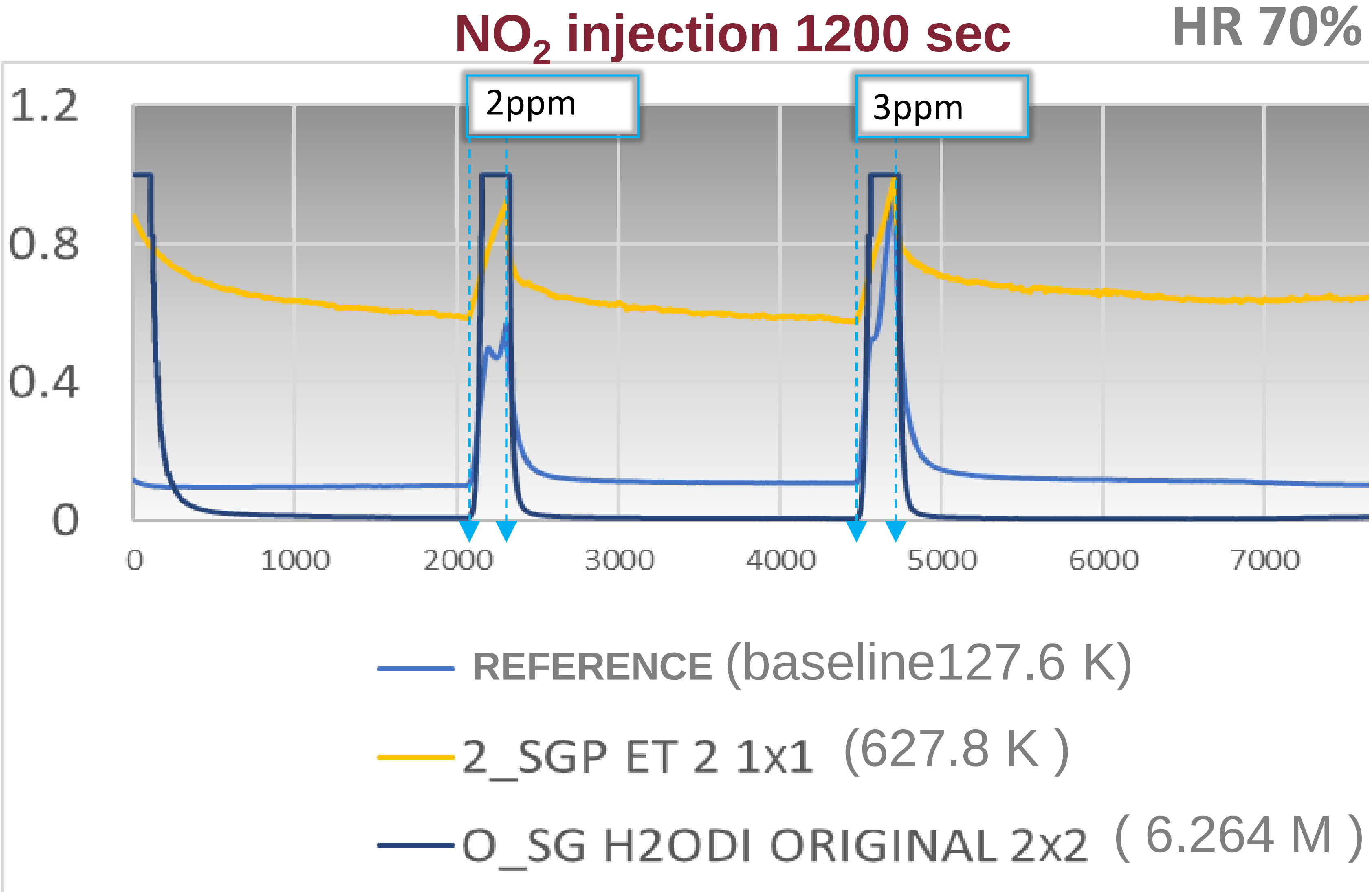
ELECTRONIC CONTACT IS MADE WITH WIRE BONDING TECHNIQUE

DROP CASTING METHOD IS USED TO DEPOSIT THE POWDERS WITH ORGANIC SOLVENTS





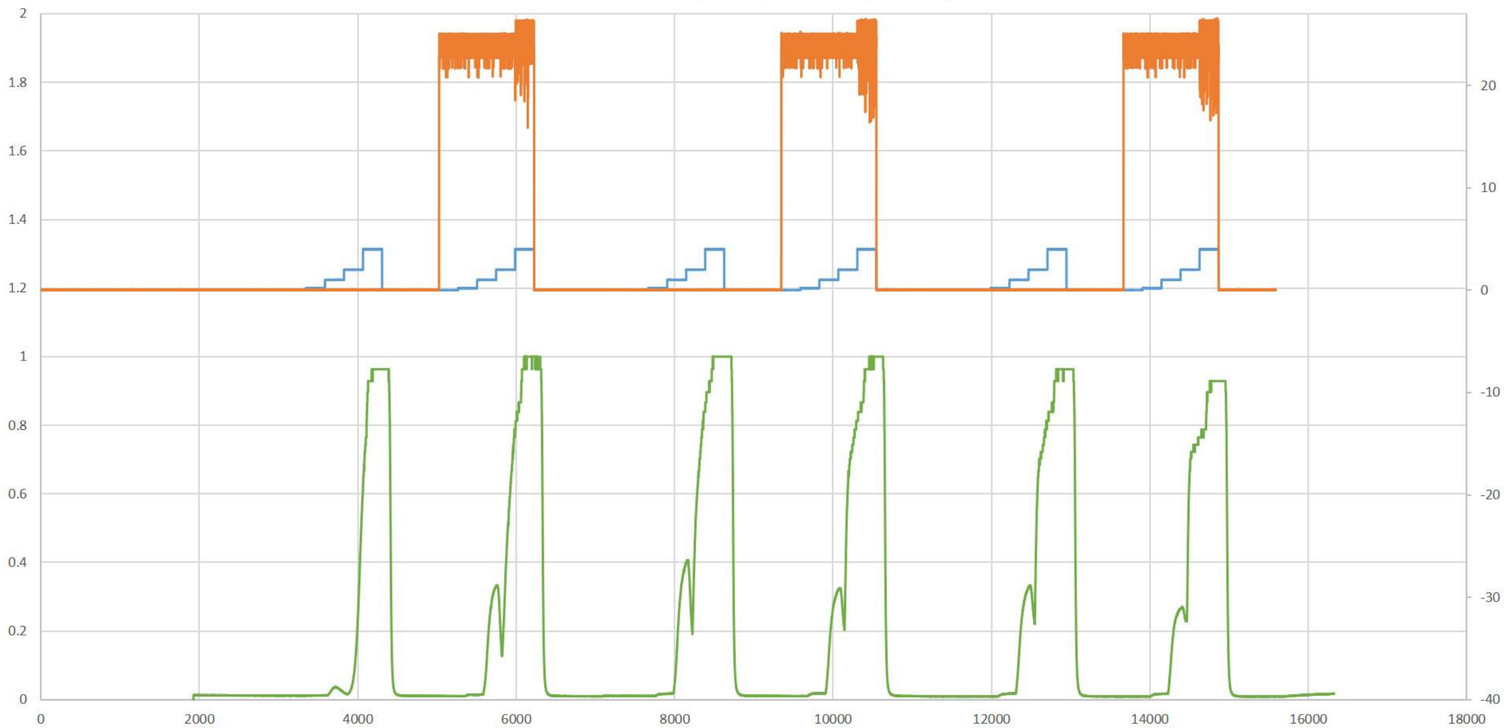
Gas Sensing


NO$_2$ injection 1200 sec
HR 70%
2ppm
3ppm
1.2
0.8
0.4
0
0
1000
2000
3000
4000
5000
6000
7000
REFERENCE (baseline127.6 K)
2_SGP ET 2 1x1 (627.8 K)
O_SG H2ODI ORIGINAL 2x2 (6.264 M)

Gas Sensing

Fluxed CO 25 ppm + NO_2 ramp 0.2, 1, 2, 4 ppm

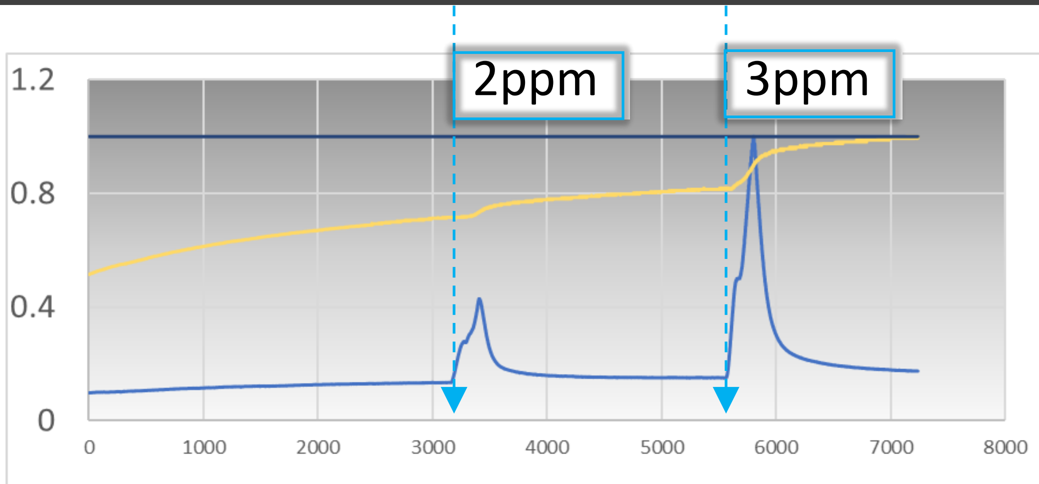
Sensor in SG below



- Low Detection Limit 0.2 and Sensitivity until 2 ppm
- Cross Selectivity **CO injection doesn't give relevant results in sensing characterization**

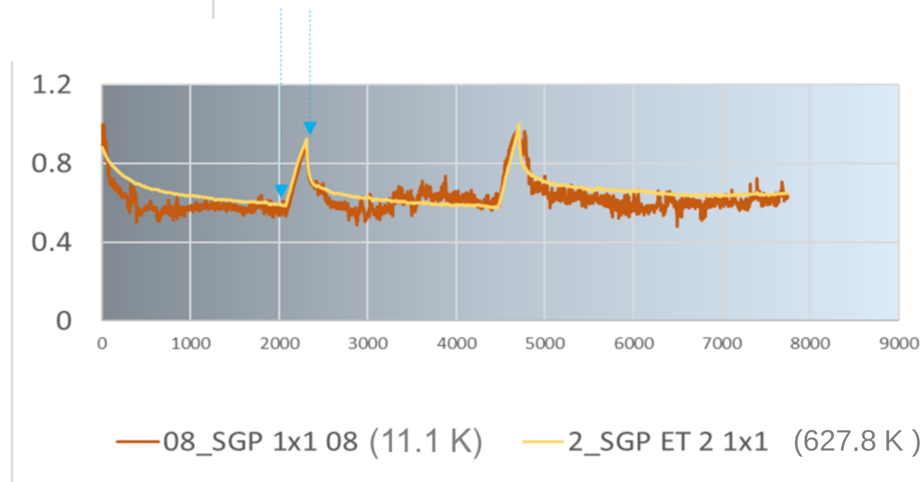
Gas Sensing

Humidity effect: 4% relative humidity to dry air



- **High performance's dependency from the humidity**
- **SGP no recovery in dry air**

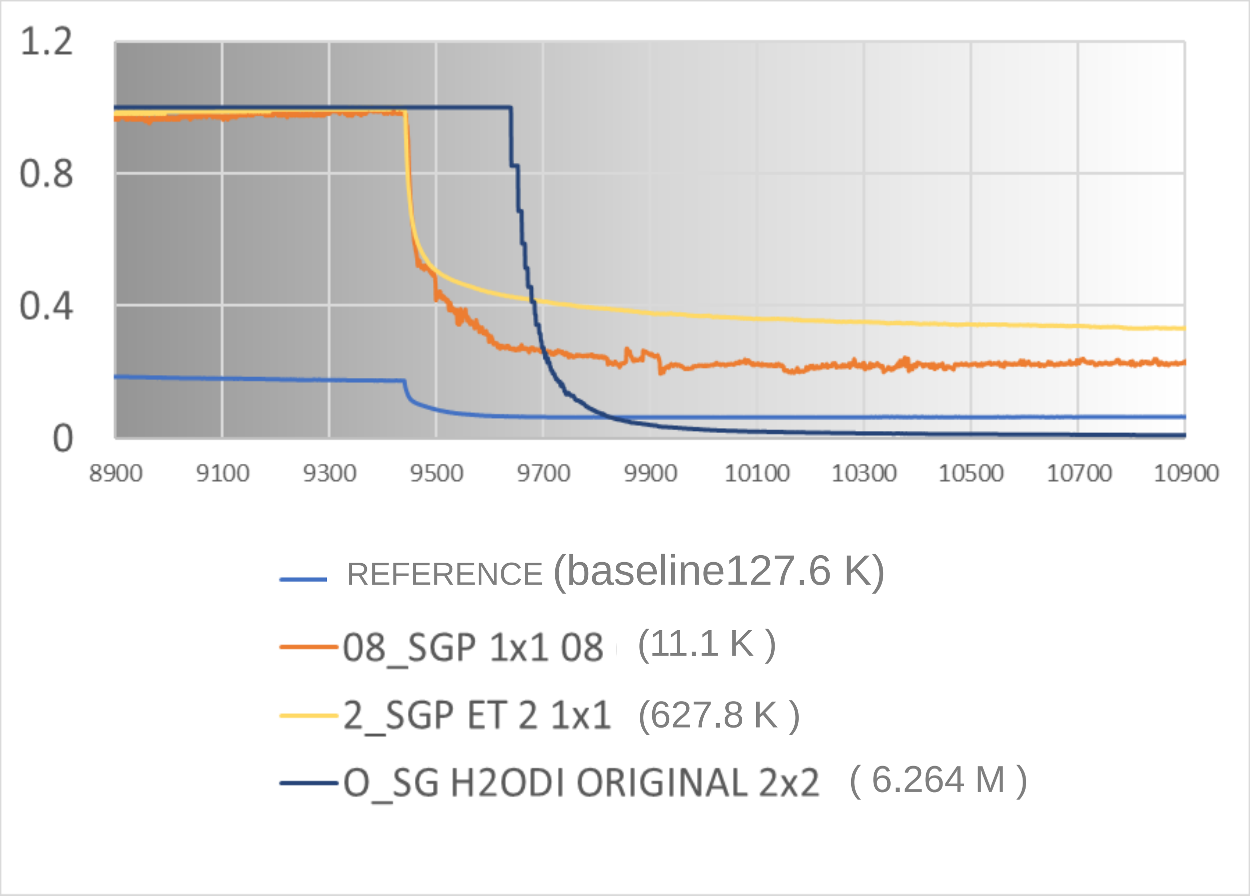
- **Influence from organic solvent used in deposition**

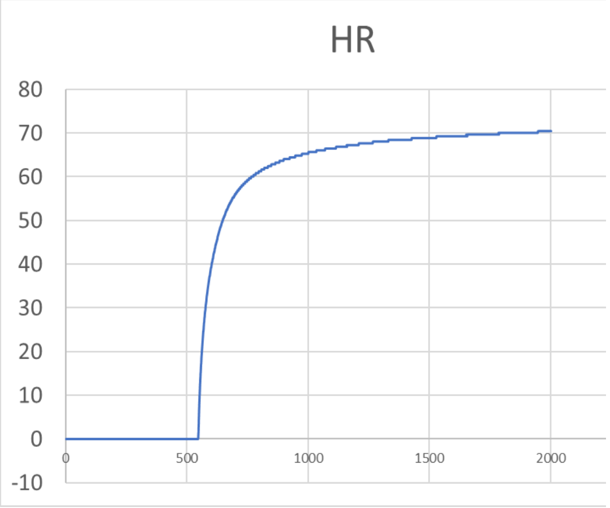


Comparing different solvents

Gas Sensing

Humidity effect: dry air to 70% wet air





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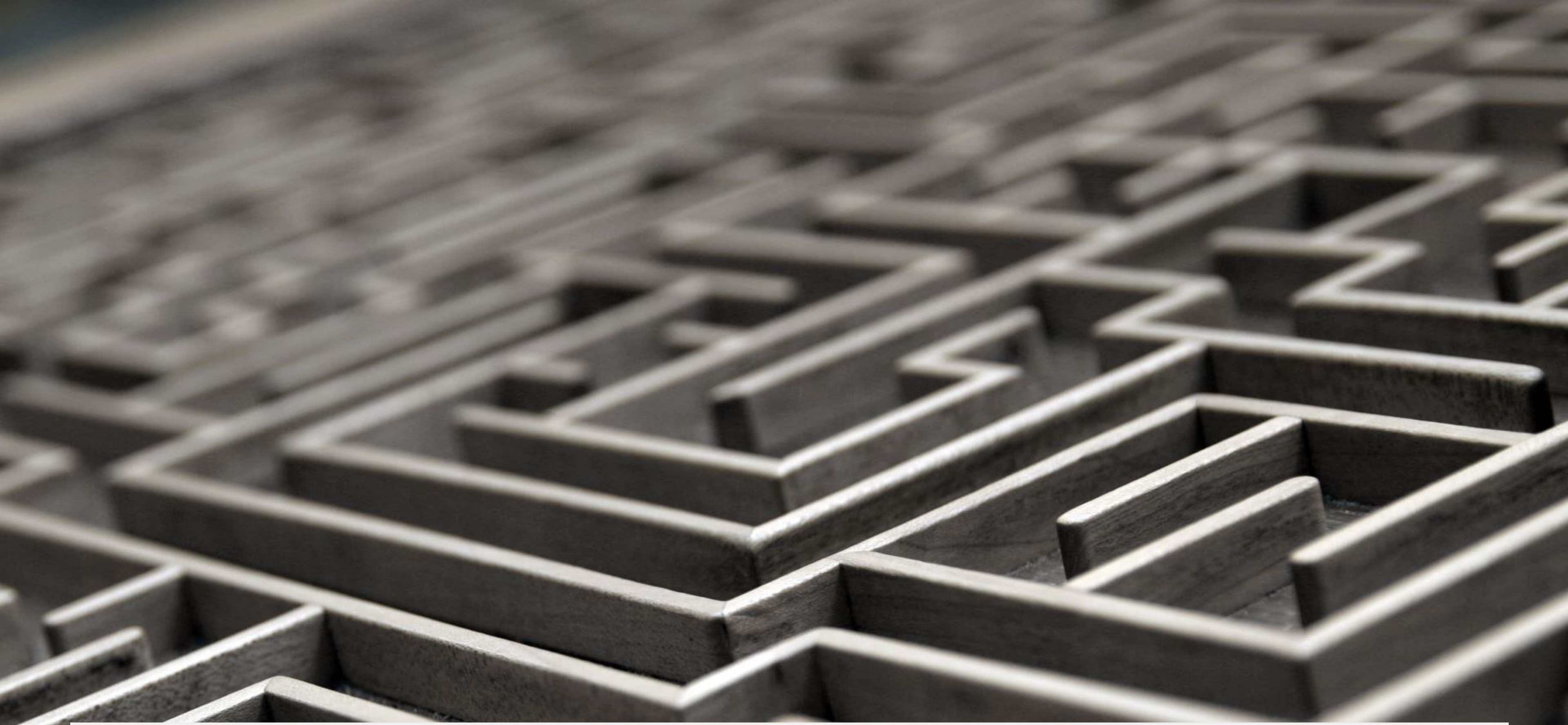

Conclusions

- Material
- Method
- Limits and perspective

From the Experimental Results

The results:

- PANI in Salt and random distribution (copolymers)
- Cassiterite and rGO
- Better recovery for SGP in wet environment

- Better response for wet environment
- Cross selectivity for NO_2

New perspective:

- To define the lower detection limit in gas sensing
- To consider inkjet printing and alternative deposition methods

People

- LEOS-Sapienza, Leonardo Mattiello, Fabiana Pandolfi, Daniele Rocco
- IMM-CNR, Alessandro Pecora
- INM-CNR, Massimiliano De Luca
- MNF-FBK, Andrea Gaiardo, Pierluigi Bellutti, Lorenza Ferrario, Alvise Spagolini, Lia Vanzetti, Giancarlo Pepponi, Evgeny Demenev
- FMFS-FBK, Victor Micheli

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Thanks for your attention