European Network on New Sensing Technologies for Air Pollution Control and Environmental Sustainability - *EuNetAir*
COST Action TD1105

Institute for Environment and Development - IDAD
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NANOTECH SENSORS FOR GAS SENSING APPLICATIONS

University of Brescia

Presenter's Name: *Giorgio Sberveglieri*

COST is supported by the EU Framework Programme
cost EUROPEAN COOPERATION IN SCIENCE AND TECHNOLOGY
EUROPEAN SCIENCE FOUNDATION ESF provides the COST Office through a European Commission contract

SENSOR

Outline

- SENSOR Lab Brescia University and CNR (**Research/Measurement/Service Facilities**)
  - A bit of history in chemical sensors
- Nanoscience and nanotechnology for chemical sensing devices
  - Preparation of metal oxide nanowire based chemical sensors
  - (SI) Surface Ionization devices
- Conclusions

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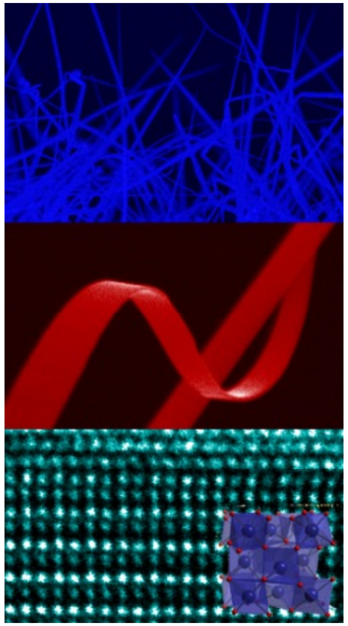
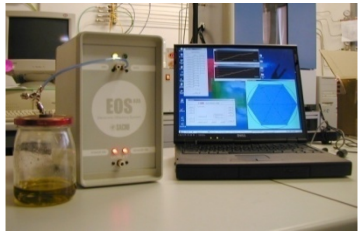
SENSOR Lab.

- SENSOR Lab. has been established in 2003 in University of Brescia Laboratory for Gas Sensors and Artificial Olfactive Systems. From 2013 it's also a Section of **CNR- INO**.

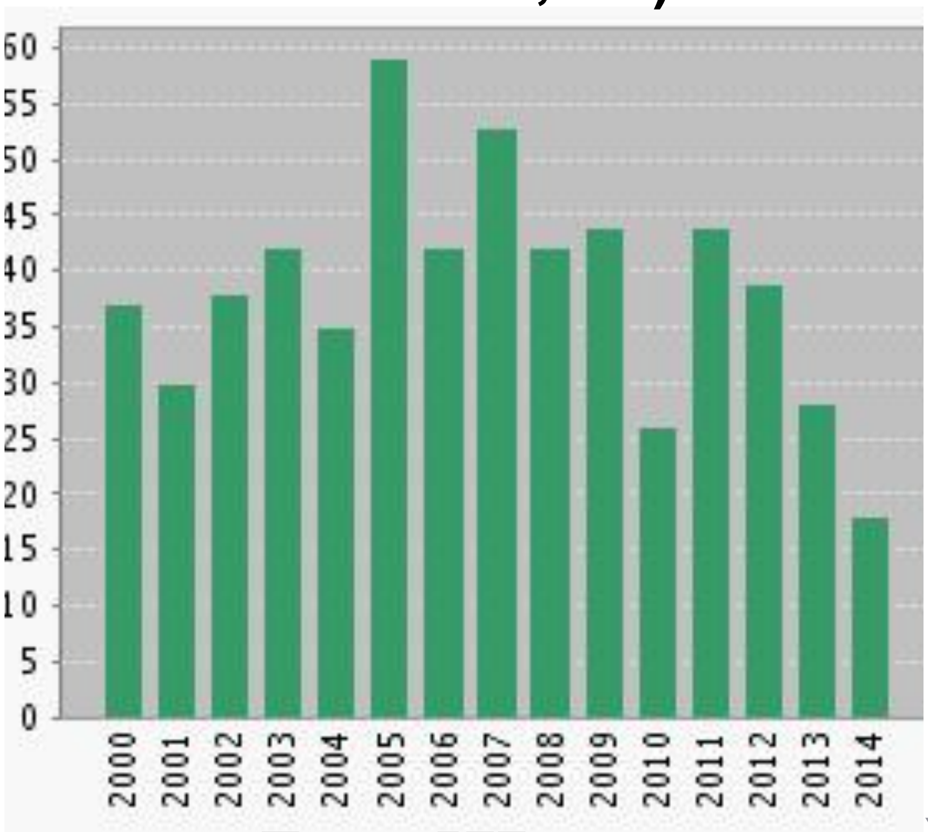
- **Mission**
  – Preparation of MOX gas sensors and advanced applications based on nanotechnology such as : **gas/flavor sensors, Artificial Olfactive Systems (AOS) , thermoelectric devices and photovoltaic,** useful in applications domain like environmental monitoring, food safety and processing control, security





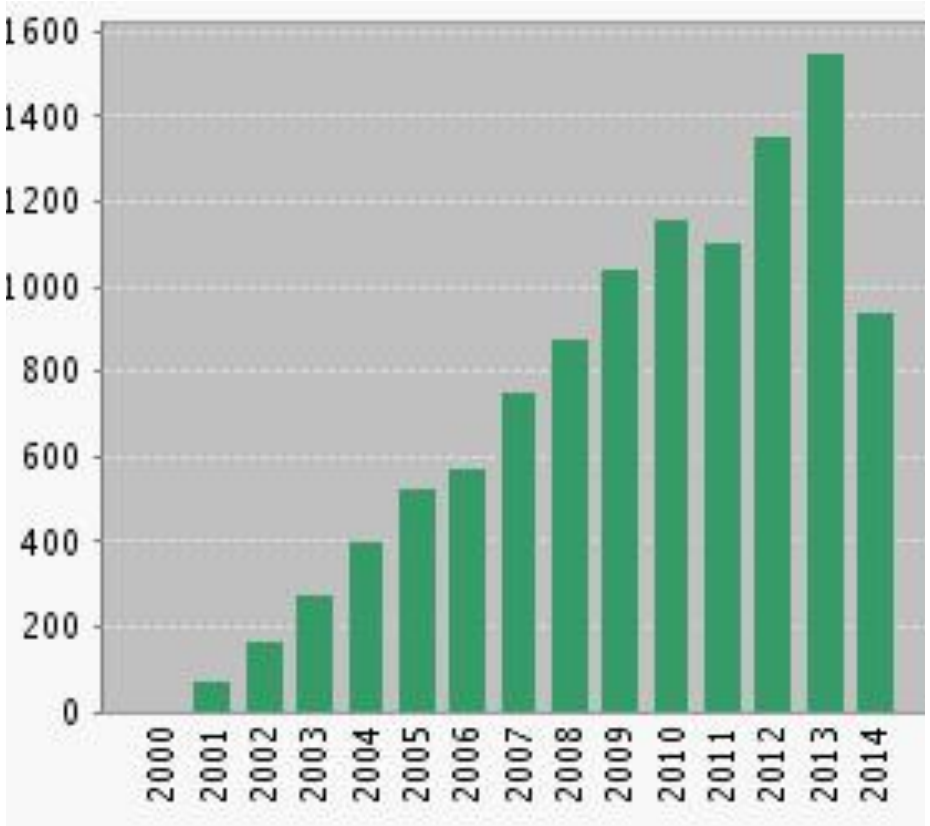
SENSOR Lab in web of science

Published papers (SCI-EXPANDED, CPCI-S, BKCI-S, CCR-EXPANDED, IC.)



Total: 577

Citations



Total: 10817
Citing articles: 7788
Average citations per item: 18.75
H-index: 48

Instrumentation and Research Facilities

Material preparation

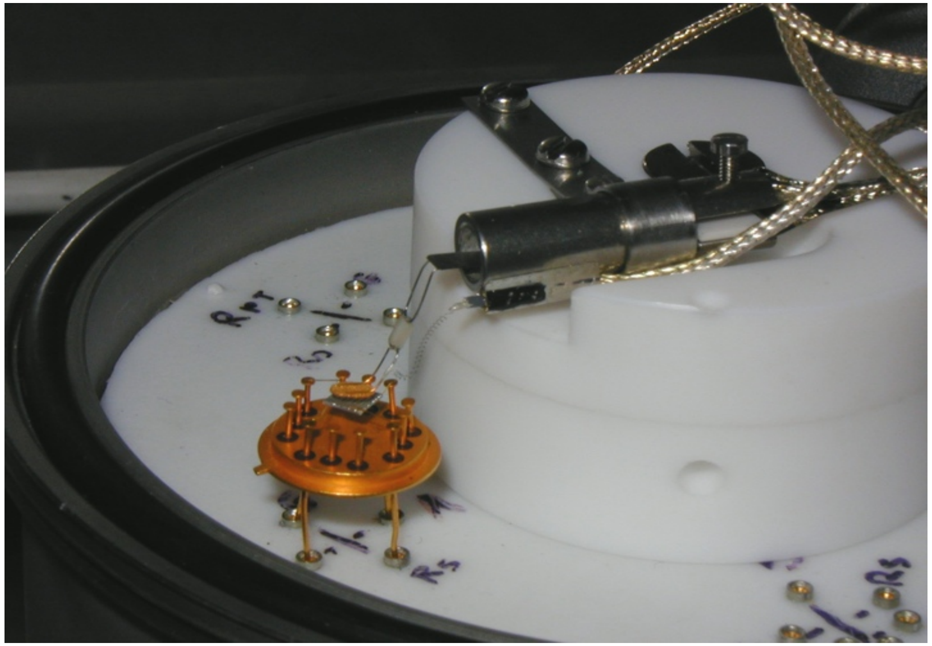
- Two magnetron Sputtering (DC and RF) with load-lock systems;
- Thermal evaporation plant with cryogenic pump;
- Spin Coating System provided with a Programmable Logic Controller;
- Three furnaces for high-temperature deposition of nanowires of metal-oxide;.

Characterization

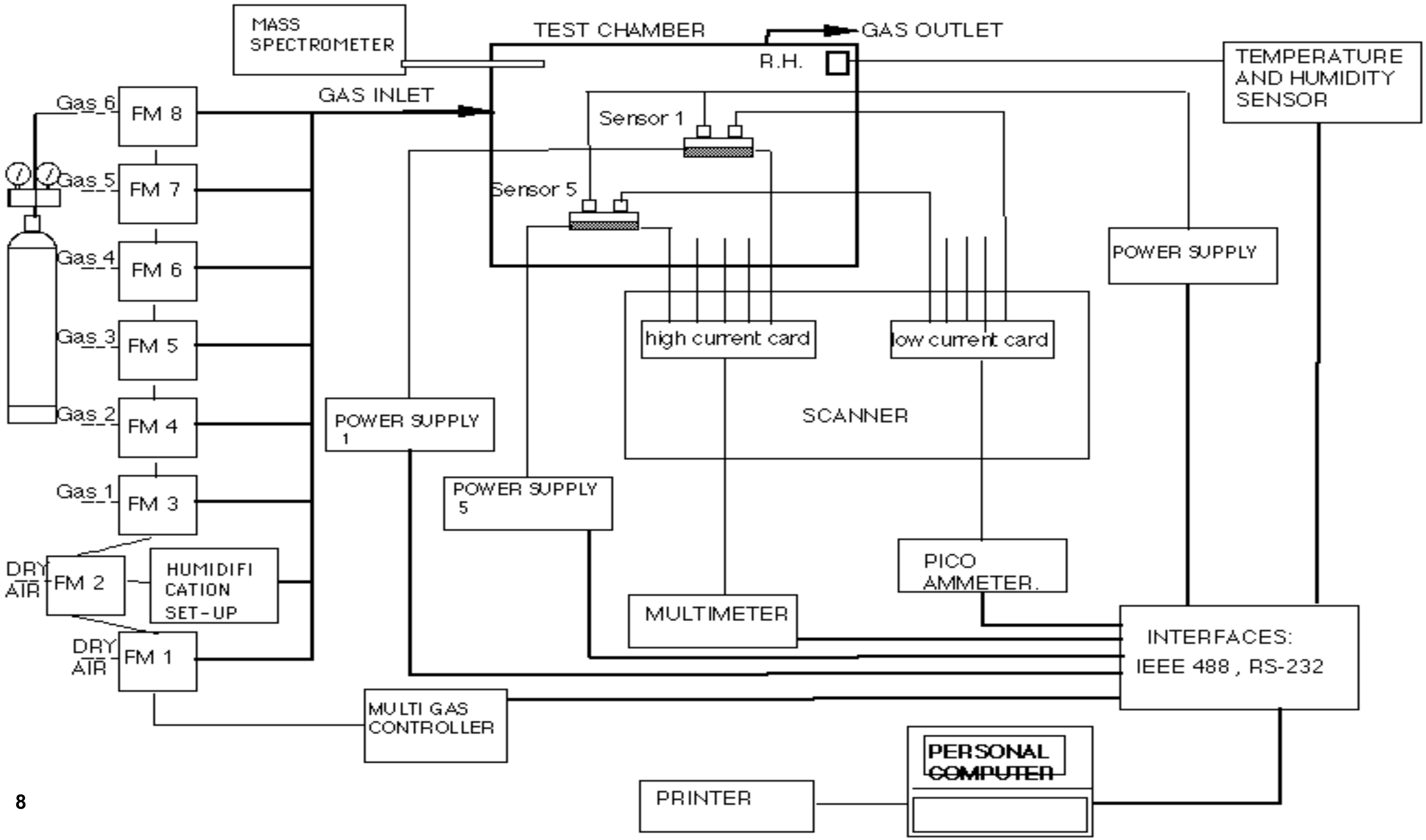
- Four advanced systems for the measurement of gas mixtures in controlled conditions of humidity, temperature and light exposure.
- Setup for solar cells characterisations (4”x4” Solar Simulator + I/V Source, VIS - UV Spectrometer)
- (AFM (LFM, NC-AFM, IC-AFM, Phase and STM) with Nanomanipulation and Material Deposition tools.
- SEM-FEG with ETD, IN-LENS, BSE, STEM EDX detectors and in-situ nanomanipulation. HR -TEM (CNR - IMM Bologna).

Kelvin Probe System

- Kelvin Probe technique (Besocke Delta Phi) is used to measure work function. The vibrating plate, made by Au, is a grid of circular shape of radius 1.2mm, piezo-electrically driven at 160Hz and placed 1mm far from the sample surface



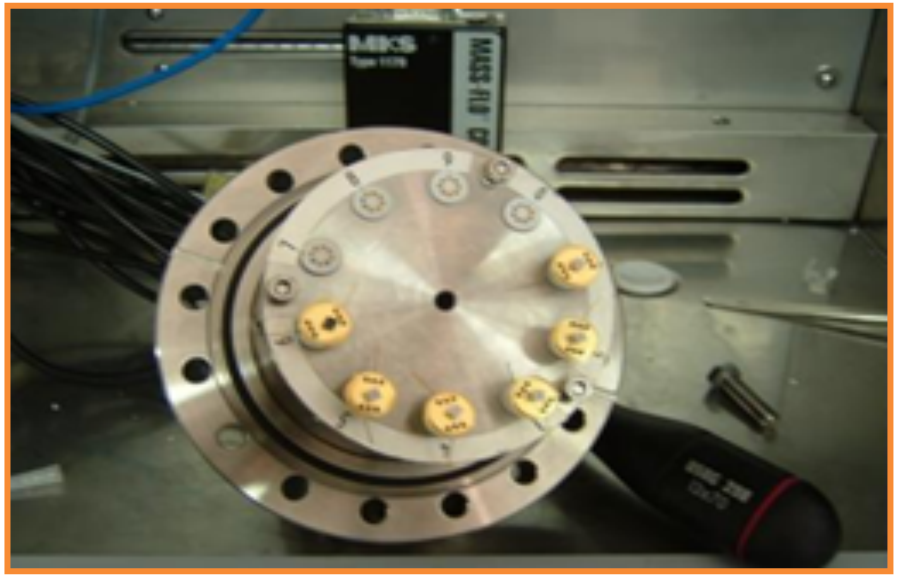
Experimental set- up for testing the sensor mixture of gases

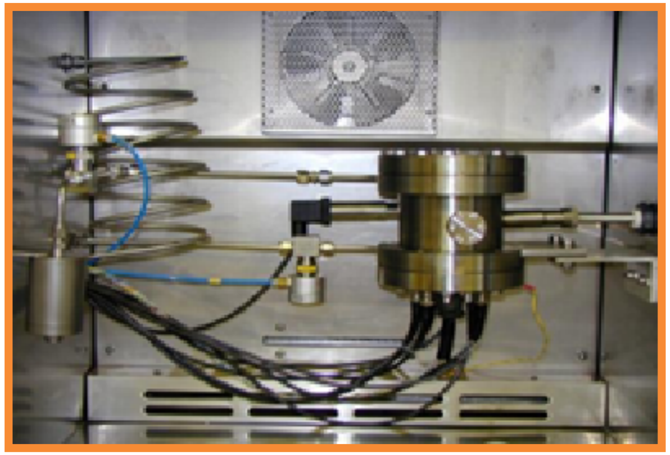


Facilities: systems for gas sensors electrical characterization

Three advanced systems for the measurement of the dc electrical response of ten sensors to six different gases in presence of relative humidity, the outlet of the test chamber is connected to a MS spectrometer. One set-up is equipped with an ozone generator and detector

The instrumentation includes a temperature-stabilized sealed chamber (volume of 1 L) at 20°C under controlled humidity. By mass-flow controllers we are able to control that the flux is constant of 300mL/min, in order to mix flows coming from gas bottles containing a certified amount of the analyte gas diluted in synthetic air with the background flow.





A selection of EU recent research projects

- **FP5** IST "Advanced gas sensing Technology for portable applications of low power gas sensors" (ADVANTAGAS) 1/1/2002 to 31/12/2005

- **FP6** Priority 3 "Nano-structured solid-state gas sensors with superior performance" (NANOS4) 1/1/2004 to 1/03/2007 – SENSOR CNR Coordinator. Partners: EADS (IND–D), VAI (IND-FI) , SAL (IND-I), SACMI (IND-I) , AOA (IND–D), UB (UNI–E), IMM-CNR (RES-I) , FhG-IPM (RES-D) , INPG (UNI-F)

- **FP6** Priority 2 (WoundMonitor) 1/2006-12/2008 Mobile system for non-invasive wound state monitoring. Main partners: Univ. Manchester (UK-RES), Biodiversity SRL, (I-IND), Umwelt-Systemtechnik GmbH (D-IND)

- Program Nanoscience In The European Research Area "Nanowire Arrays For Multifunctional Chemical Sensors Nanosci-Era" (NAWACS) 1/2007-12/2009 .

- **FP7** NMP-2009-1.2-3 Nanotechnologies – coordinated call with Russia (S3) "Surface ionization and novel concepts in nano-MOX gas sensors with increased Selectivity and Stability for detection of low concentrations of toxic and explosive agents" SENSOR CNR Coordinator project started on Sept. 1st 2009.

A selection of EU active research projects

- **FP7**, SEC-2012.3.4-4 “Sniffer for concealed people discovery ” (SNOOPY) 1/1/2014 to 31/12/2016. Partners: Univ. of Brescia (UNIBS – coordinator), CNR-INO SENSOR Lab (CNR), University of Rome Tor Vergata (UTOV), AIRBUS group (AIRBUS), C-TECH Innovation Ltd. (C-Tech), Center for Security Studies (KEMEA)

- **FP7**, FP7-PEOPLE-2011-IRSES “Oxide Nanostructures for Wireless Chemical Sensing” (WIROX). 01/01/2012-31/12/2015. Partners: Univ. of Brescia (Coordinator), CNR INO SENSOR Lab, Univ. Koeln, FORTH, IREC, INRS, CSIR, QUT

- **FP7**, FP7-PEOPLE-2013-IRSES “Innovative interfaces for energy-related applications” (INTERNEW). 01/01/2014-31/12/2017. Partners: CNR INO SENSOR Lab, INRS, Univ. Zaragozza, UJI, CNRS, IPE, INRS, CNEA, SNU

- **FP7**, FP7-PEOPLE-2011-IOF “Förster resonant energy transfer for high efficiency quantum dot solar cells” (F-LIGHT). 01/09/2012-31/08/2015. Partners: CNR INO SENSOR Lab, INRS

- Multi Sensor Platform (MSP) for Smart Building Management GA 611887; Unione Europea programma FP7-ICT-2013-10 Heterogeneous Integration and take-up of Key Enabling Technologies for Components and Systems, 01/09/2013-31/08/2016

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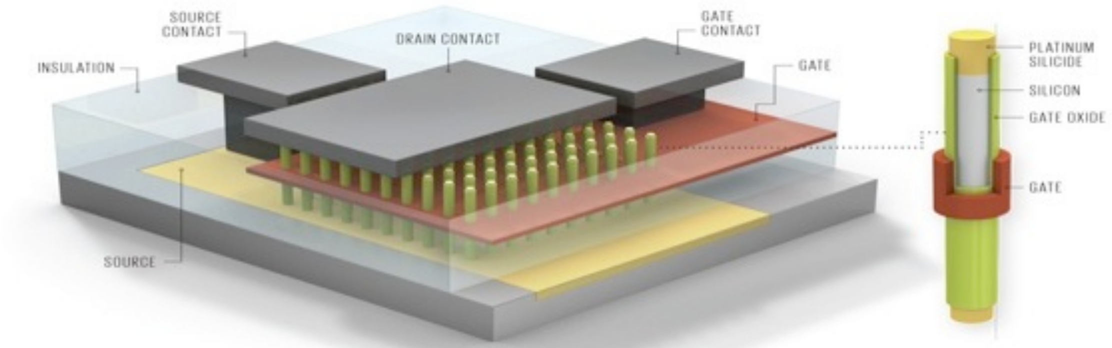
Proposal submitted in H2020 in 2014

- **FOODSENS:** Integrated food processing control for enhanced product safety and process efficiency . CNR INO Coordinator (CNR)
- **ORACLE:** Quantum dot-**OR**ganic donor-**AC**ceptor architectures with pi-extended optically control**LE**d bridges for new generation computing (UNIBS)
- **CATHEDRA:** **C**ooperation in **A**pplied research and **Tec**H**nology transfer between **E**u**R**ope and **A**merica (CNR)
- **TEAMING:** Establishment of a performant and competitive Centre of Research and Innovation Excellence in Sensor Technology, in Bucharest, Romania (CNR)
- **MANTELS:** Multi-layered inspection technologies for secure and efficient large volume freight supply chains (CNR)

Miniaturization

- Moore's Law for the advancement of integrated circuits followed since 1960s.
  - Nowadays researchers push nanolithography technology to its extreme limits to reduce the footprint of electronic devices,
- Nanowires have already brought fundamental changes to the future of the IC industry and will possibly allow keeping up with Moore's Law.
  - logic circuits, sensing and active elements for highly sensitive bio/chemical/photon sensors.
  - reliable and economic scaled-up processes that integrate nanowires into electronic devices.
    - This challenge needs to be urgently met if nanotechnology has to evolve beyond the academic interests.



Nanowire Transistors Could Keep Moore's Law Alive

By Alexander Hellemans

Illustration: Emily Cooper

Gas Sensors

- Chemical or biological substances detection
- Monitor industrial processes
- Spoilage of food and toxic reagents during production
- Essential development scientific methods to assess, model and analyze exposure levels to potentially toxic compounds
- Measured gases are complex odor consisting in a mix of different analytes
  - Gas sensors arrays or electronic olfaction systems
- Chemiresistors simple architecture and easy signal processing

MOX chemical sensors

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- Metal-oxides represent a category of materials with diversified properties covering all aspects of material science and physics in areas including superconductivity and magnetism
- Metal oxides are already well established in the field of gas sensing
  - sensing mechanism: **electrical resistance variation** upon gas chemisorption
- In 1991 Yamazoe showed that **reduction of crystallite size** went along with a significant increase in sensor performance.

MOX gas sensors

- Technological challenge:
  - fabrication of materials with **small crystallize size** which maintained their stability over long term operation at high temperature
- A huge variety of devices have been developed mainly by an empirical approach and a lot of basic theoretical research and spectroscopy studies have been carried out to improve the well known “3S” of a gas sensor
  - Sensitivity, Selectivity and Stability

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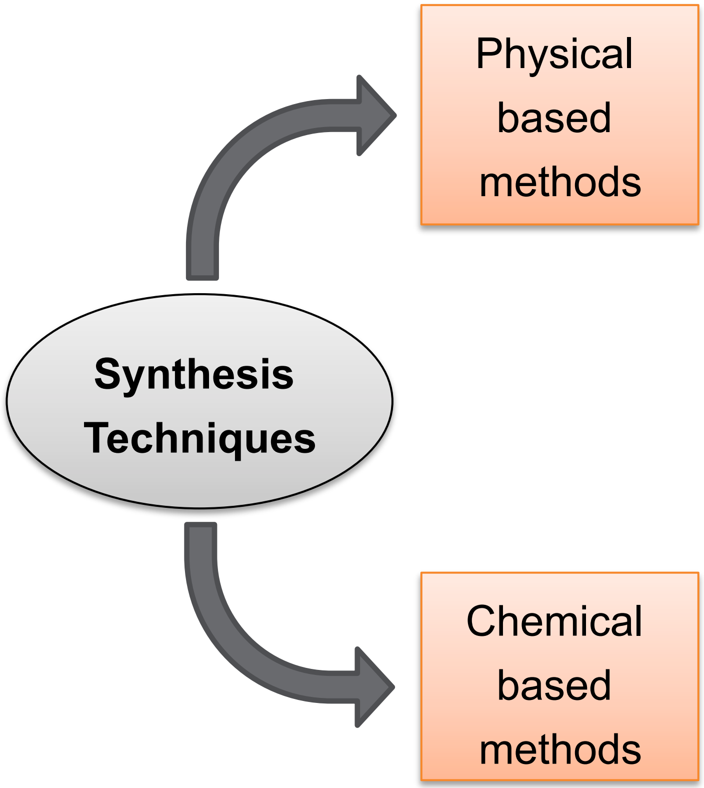
Why MOX NWs for chemical sensors

- Very large surface-to-volume ratio
- Downsizing of sensing materials improves the sensor performances
- Dimensions comparable to the extension of surface charge region
- Stability (high degree of crystalline order)
- Simple and low-cost preparation methods

Preparation techniques

- Two well-known and contrasting design strategies: top-down and bottom-up
- **Top-down** technologies are the staple of IC manufacturing and the semiconductor industry (lithography, thin-film deposition and etching)
- **Bottom-up** strategies is a more natural approach and provide many attractive qualities. To capture the advantages of both methodologies:
  - bottom-up synthesis of NWs with uniform size and consistent performance,
  - assembly into highly ordered arrays that can interface with top-down fabrications

Bottom –up Synthesis Techniques



MOx nanostructures grow along a preferential direction, thanks to internal or external physical forces.

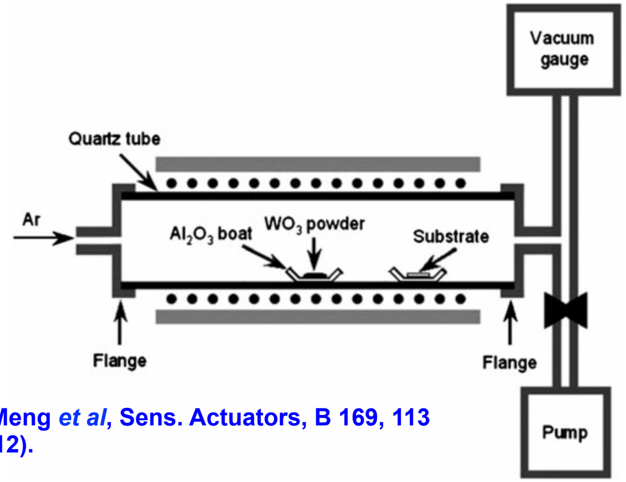
- **Physical Vapour Deposition**
- **Electrospinning**
- **Pulsed Laser Deposition**
- **…**

Chemical reactions are dominating the growth process.

- **Chemical Vapour Deposition**
- **Thermal Oxidation**
- **Hydro & Solvothermal Growth**
- **Sol-Gel Synthesis**
- **…**

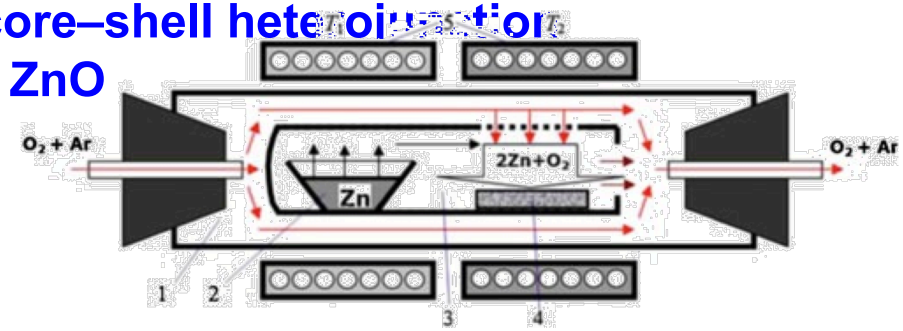
Physical and Chemical Vapour Deposition

- In PVD, MOx powder is evaporated in a furnace at very high temperatures, in vacuum or at ambient pressure.
- Fabricated nanostructures:
  - SnO_2, ZnO, In_2O_3, WO_3 and $W_{18}O_{39}$
  - SnO2–ZnO heterojunctions
  - ZnO Surface-coated with organic modules

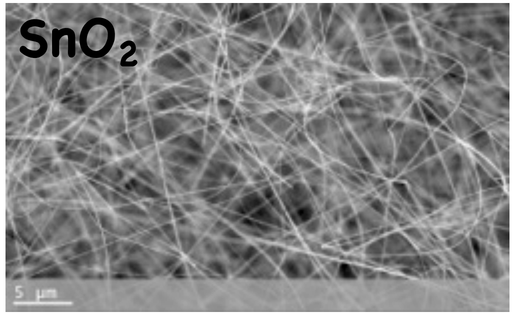


D. Meng *et al*, Sens. Actuators, B 169, 113 (2012).

- CVD technique consists in the reaction of volatile precursors flowing in the chamber for the production of MOx compounds on the substrates
- Fabricated nanostructures:
  - ZnO, In_2O_3, TiO_2 and SnO_2
  - Cr_2O_3–ZnO core–shell heterojunction
  - Metal-doped ZnO

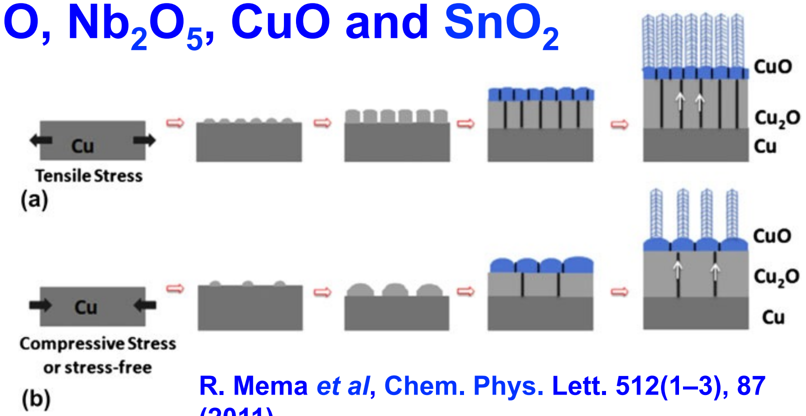


O. Lupan *et al*, Mater. Res. Bull. 45(8), 1026 (2010).

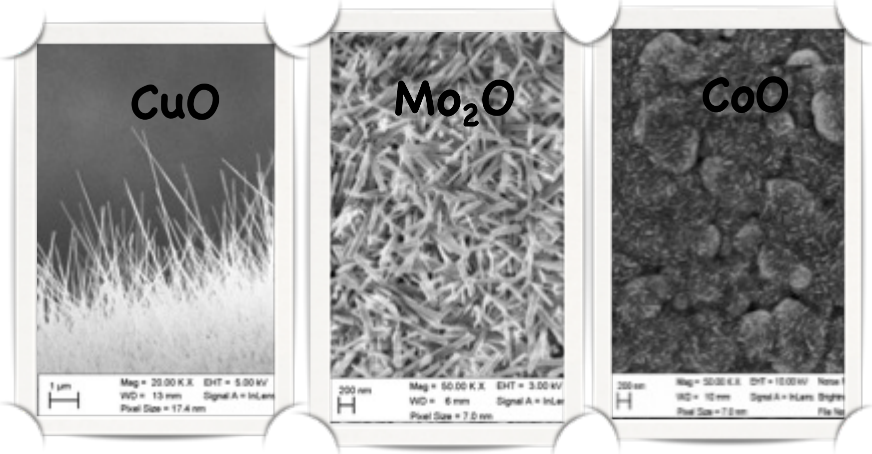


Thermal Oxidation and Electrospinning

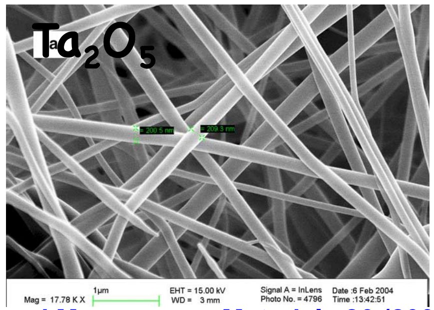
- **Thermally assisted oxidation of a metal layer or stub in an oxidizing atmosphere.**
- **Fabricated nanostructures:**
    - **ZnO, Nb_2O_5, CuO and SnO_2**



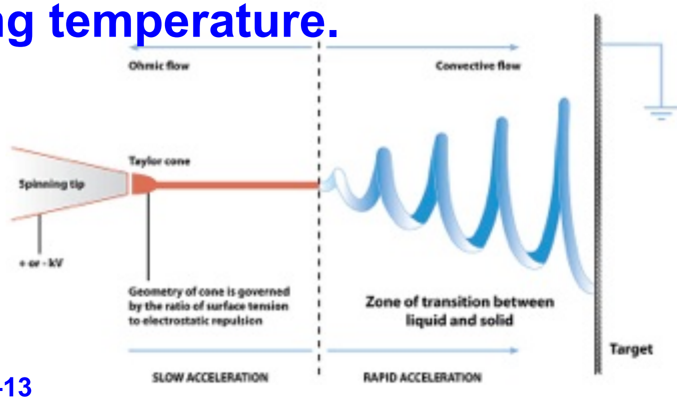
R. Mema *et al*, Chem. Phys. Lett. 512(1–3), 87 (2011).



- **Electrospinning technique uses an electrical charge to fabricate very fine wires from a liquid.**
- **High temperature is not required to produce the nanostructures and thus is a very attractive synthesis method at low fabricating temperature.**
- **Fabricated nanostructures:**
    - **ZnO, TiO_2 and SnO_2**



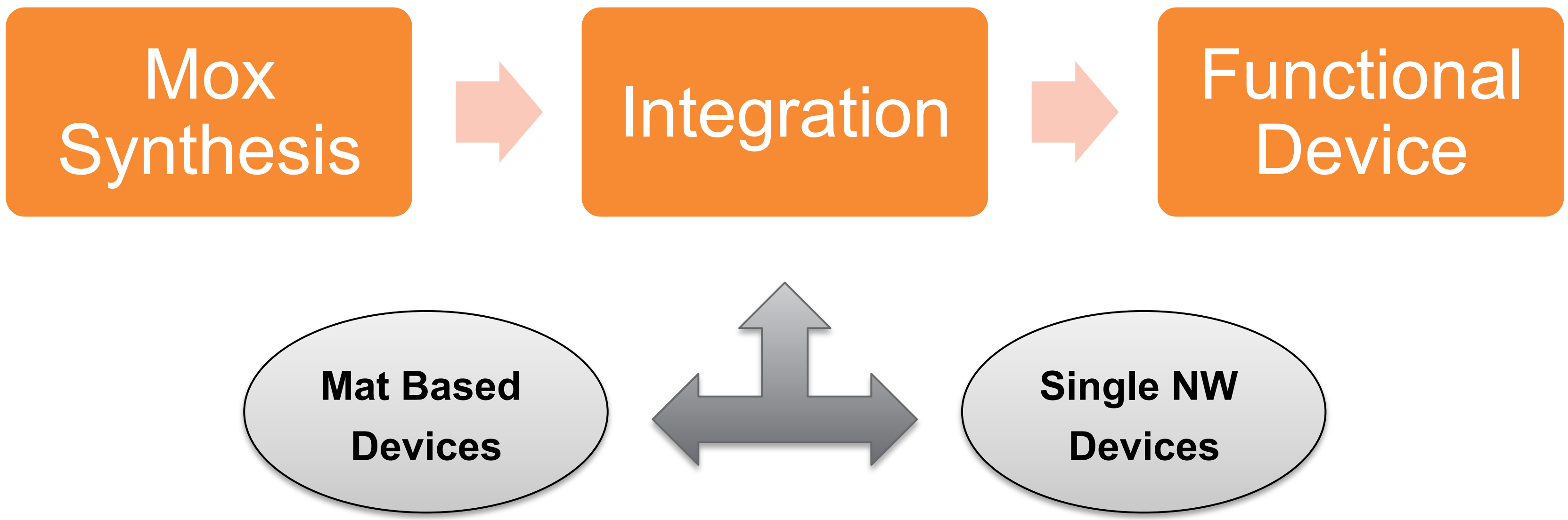
Minedys Macías et al, Microporous and Mesoporous Materials 86 (2005) 1–13



Source: wikipedia

Integration into functional devices

- **Integration strategy is strongly related to synthesis process.**

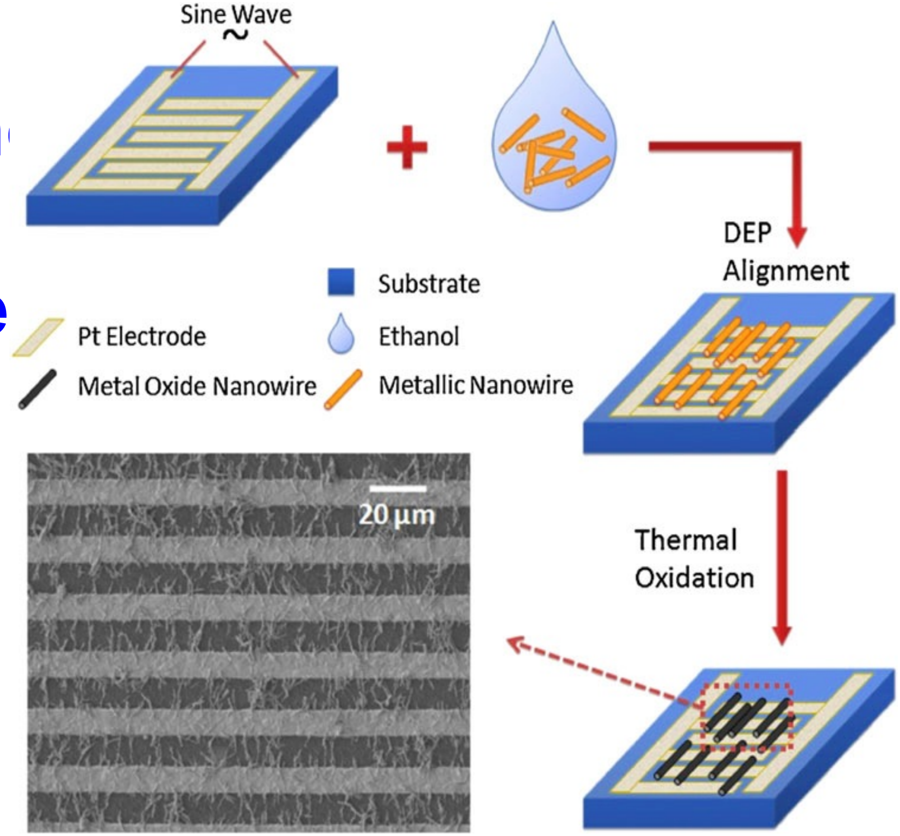


- **Conventional techniques:**
  - **Metal deposition**
  - **Silver gluing**
  -

- **Alignment is critical.**
- **Expensive techniques:**
  - **Focused Ion Beam**
  - **Electron Beam Litography**

Mat-based Devices

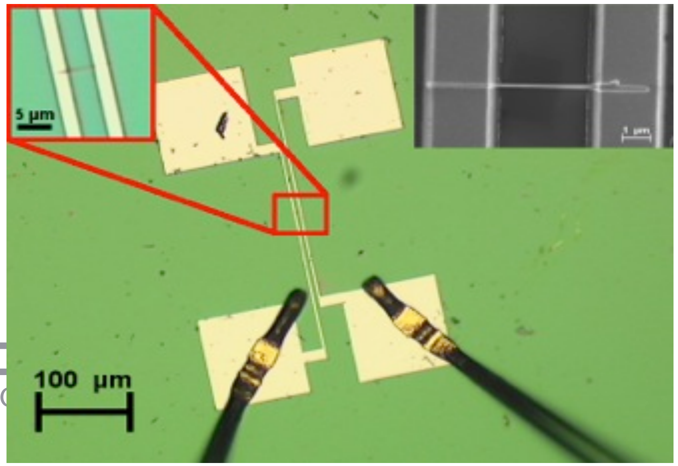
- Electrodes are required to fabricate functional mat-based devices.
- Different tecniques could be use:
  - ✓ Thermal metal evaporation
  - ✓ Shadow-masking sputterin
  - ✓ Silver glue
  - ✓ Lithography (Optical or Ele
  - ✓ Electrophoresis

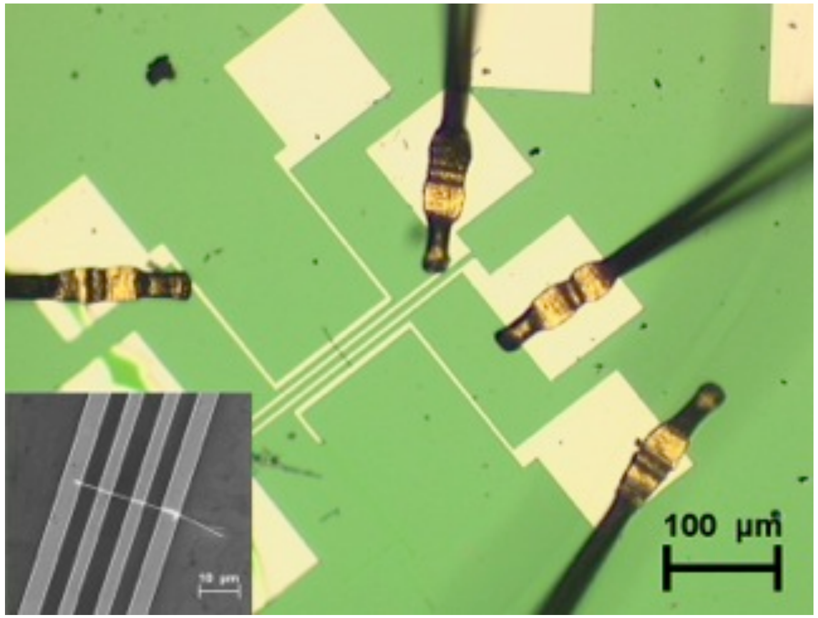


Schematic diagram of sensor chip fabricating procedure using dielectrophoresis and top view of the sensor chip surface. X.P. Li *et al*, Sens. Actuators, B 158(1), 199 (2011).

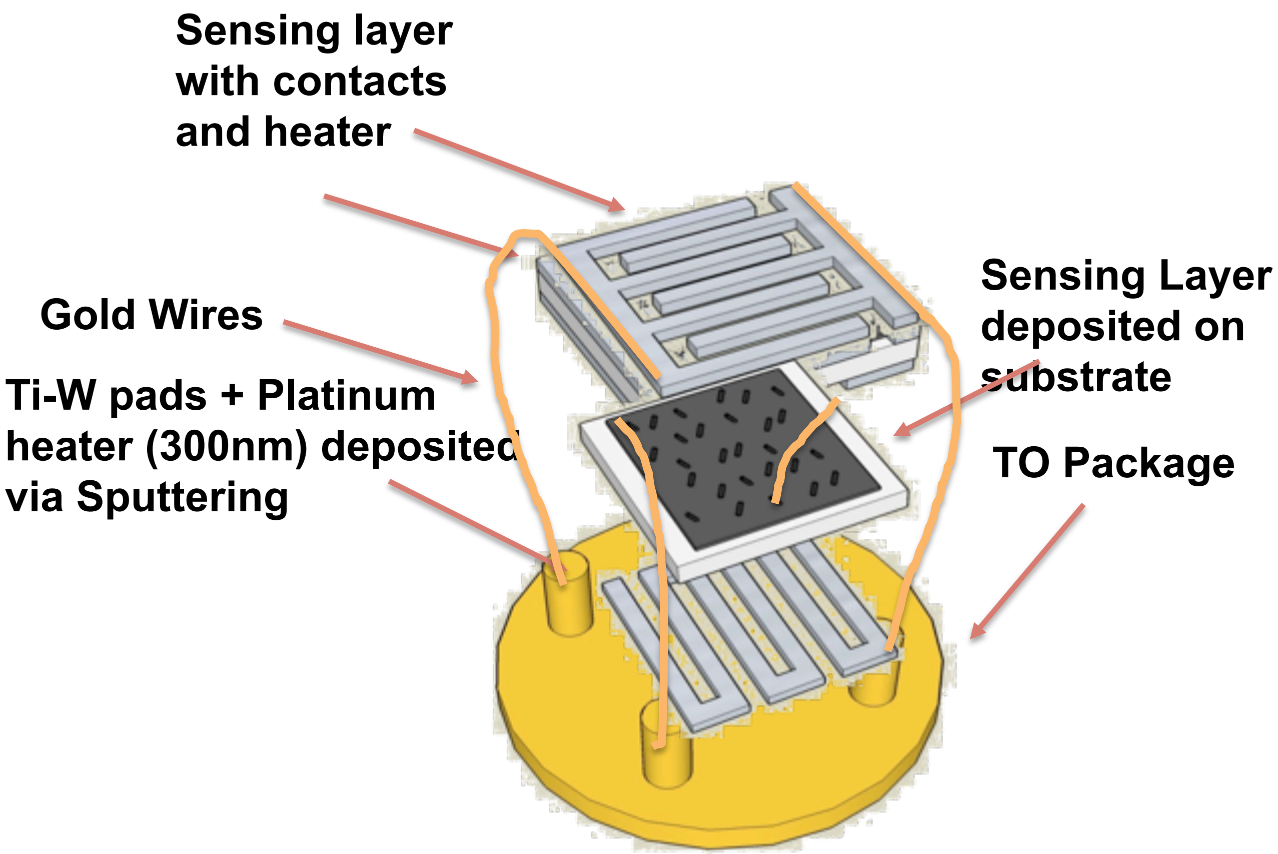
Single NWs Devices

- Single NW Devices are much more complex and expansive to fabricate.
- Alignment is very crucial, because it could be difficult to locate a single nanowire on the substrate.
- Some tecniques could be use:
  - ✓ Electron Beam Lithography
  - ✓ Electrophoresis
  - ✓ Focused Ion Beam



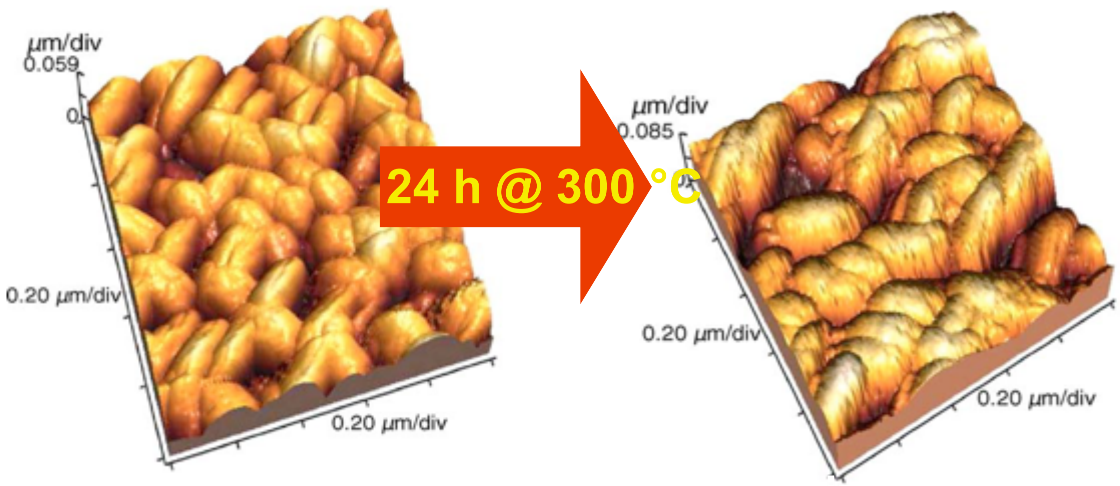


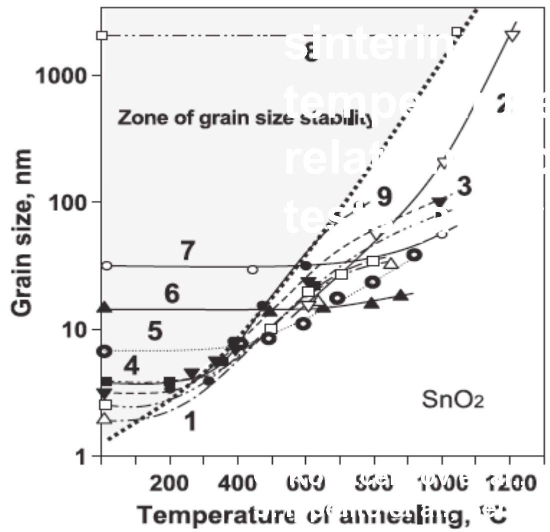
Mats NWs Chemical Sensors



Stability

Stability - thermal effects





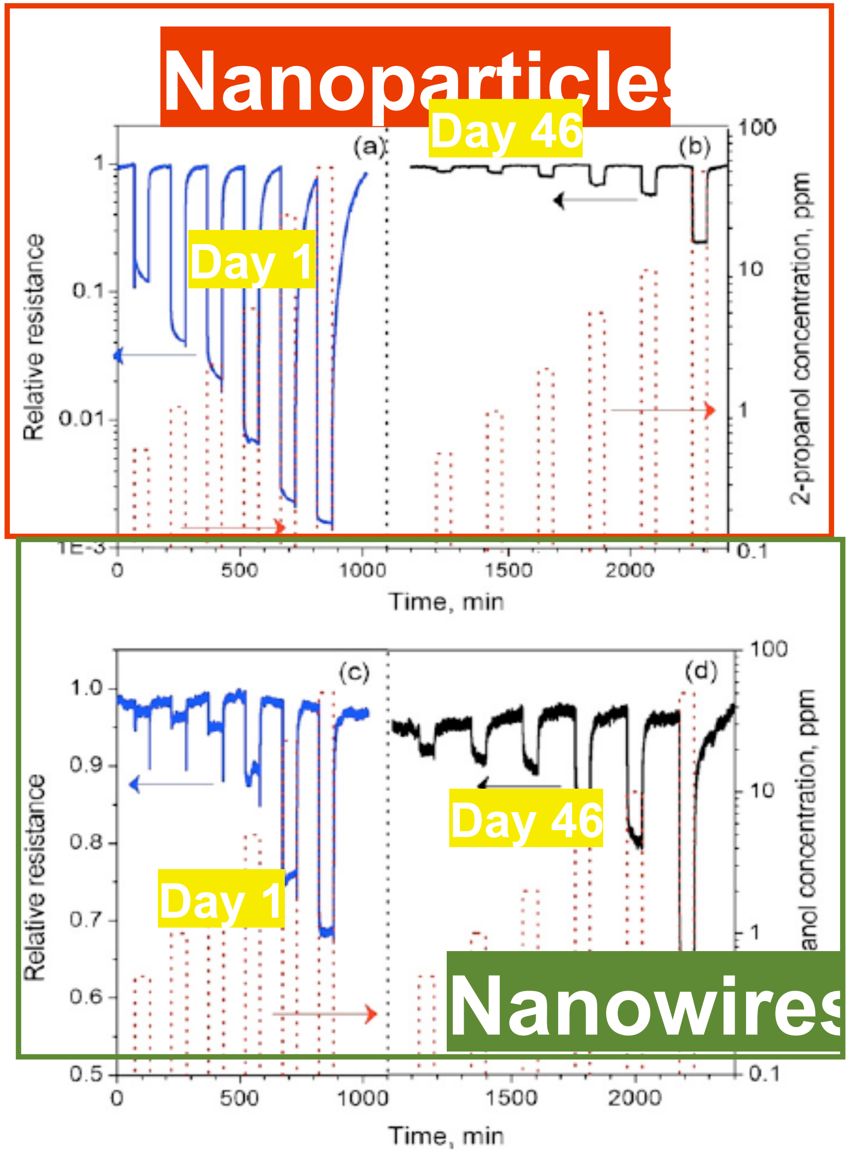
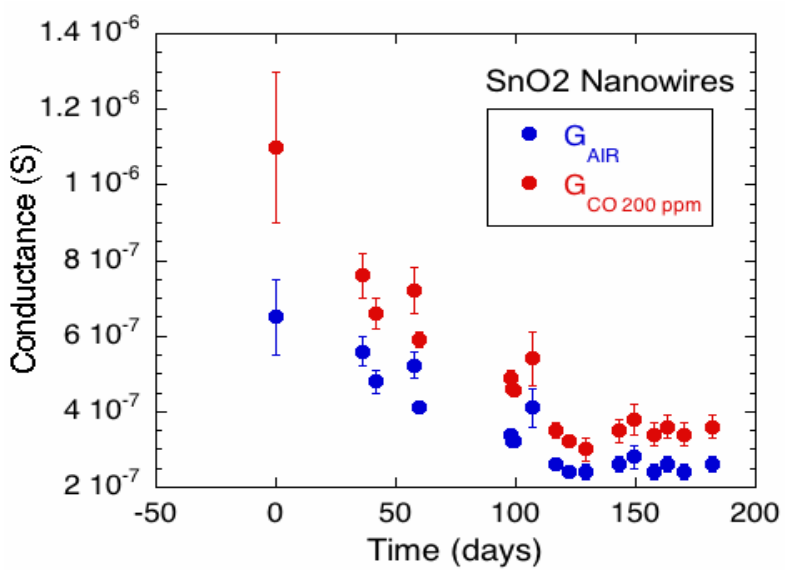
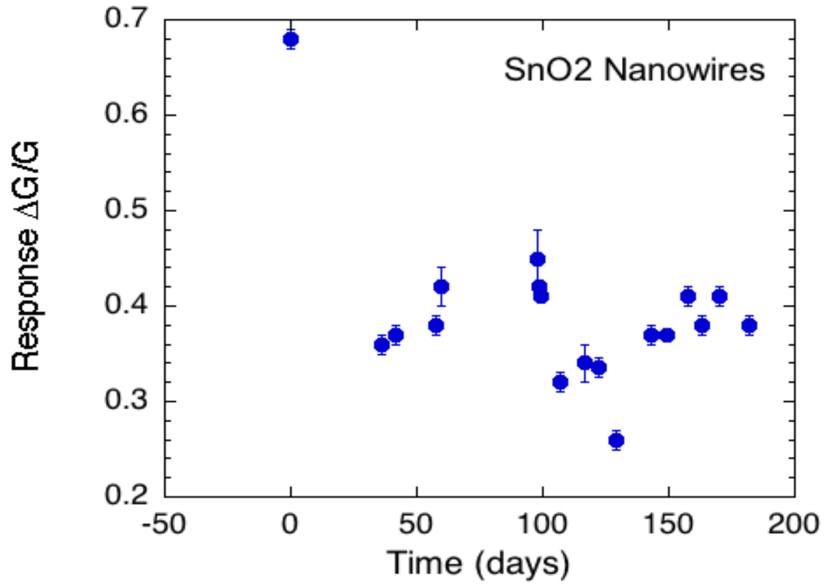


Fig. 2. The change of the SnO_2 nanostructures resistance of median sensor segment relative to the maximum value under the exposure to 2-propanol vapors of step changed concentration at 1st day (a and c) and 46th day (b and d): (a and b)—NP 3-D layer; (c and d)—NW 2-D mat.

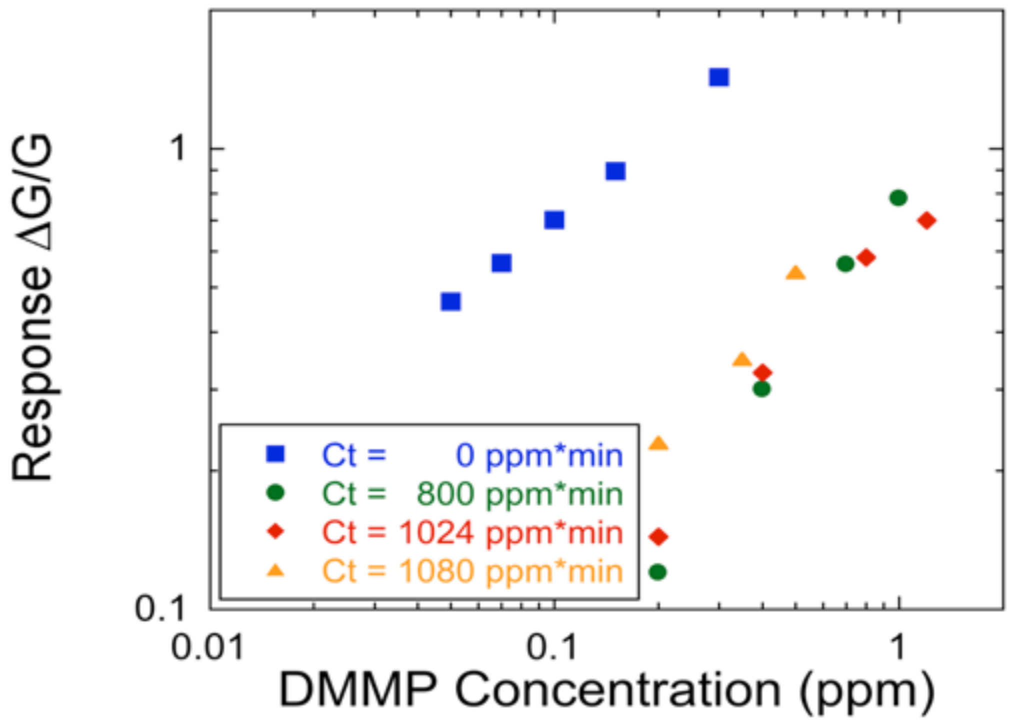
Stability - thermal effects





We used CO to test the thermal stability of gas sensors because CO exhibit almost no poisoning effects;
Both the baseline and the conductance value during gas exposure (CO 200 ppm) exhibit a similar drift toward lower values during the first 100 days, then both reach a steady state;
No drift is observed for sensor response ΔG/G, which is better described by means of a mean value and its std: ΔG/G =0.38 ± 0.05.

Stability - DMMP poisoning effects



- **Background from catalysis field:**
  - **DMMP dissociates over the oxide surface leaving phosphorous compounds that poison the catalyst layer decreasing its capability to further decompose DMMP**
  - **Poisoning effects observed working with 1000 ppm for 10 hours, corresponding concentration per time values Ct ≈ 10^6 ppm*min**

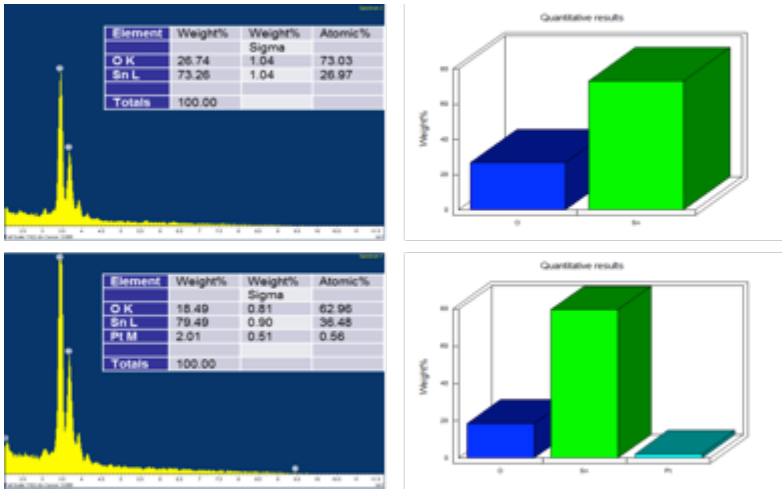
❖ **Gas sensor field**
  - **the initial capability to respond to 30 ppb of DMMP decreases with exposure to DMMP till reaching a steady state regime**

Sensitivity/ Selectivity

Giorgio Sberveglieri

Surface functionalisation

- Metal particles were deposited by magnetron sputtering on top of SnO_2 NWs, in different atomic weight ratios: 0%, 1% and 3%.
- EDX performed on samples:
    - Pt 1% --> 1.2%
    - Pt 3% --> 2.6%



Element	Weight%	Weight% Sigma	Atomic%
O K	26.74	1.04	73.03
Sn L	73.26	1.04	26.97
Totals	100.00		

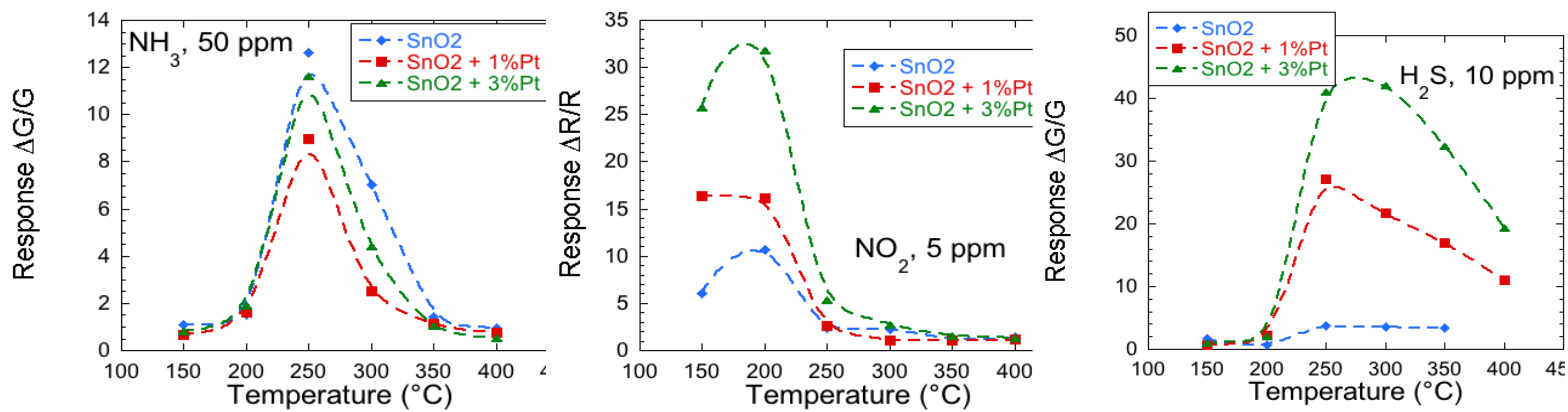
Pt 0%

Element	Weight%	Weight% Sigma	Atomic%
O K	18.49	0.81	62.96
Sn L	79.49	0.90	36.48
Pt M	2.01	0.51	0.56
Totals	100.00		

Pt 3%

Electrical Measurements

- Response to NH_3
  - Optimal temperature (250°C) is not influenced by the metal functionalization
  - Influence of metal is almost negligible
- Response to NO_2 and H_2S
  - Increasing the Pt ratio on SnO_2 NWs samples has a positive effect on sensing performances



Conductometric chemical sensors **NWs** based for the detection of Chemical Warfare Agents

❖

Toxicity Values[1]

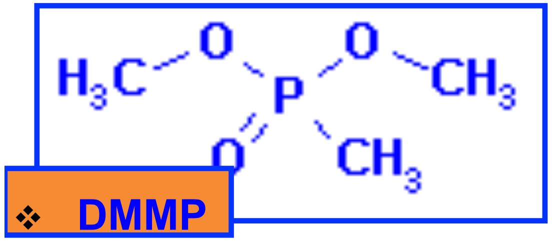
GAS	Molecular Formula	Gas type	OSHA PEL-TWA[2] (ppm)	IDLH[3] (ppm)
Nitrogen dioxide	NO_2	TIC	3	20
Carbon monoxide	CO	TIC	50	1200
Hydrogen sulphide	H_2S	TIC	10	100
Ammonia	NH_3	TIC	50	300
Tabun (GA)	$C_5H_{11}N_2O_2P$	Nerve	-	0.03
Sarin (GB)	$C_4H_{10}FO_2P$	Nerve	-	0.03
Soman (GF)	$C_7H_{16}FO_2P$	Nerve	-	0.008
Hydrogen cyanide (AC)	HCN	Blood	-	50
Lewisite (L)	$C_2H_2AsCl_2$	Blistering	-	3.5
Sulfur mustard (HD)	$C_4H_8Cl_2S$	Blistering	-	1.5

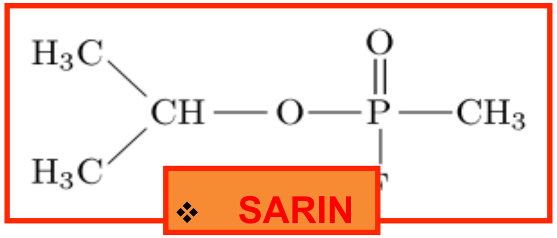
1. **Source: Y. Sun, K.Y. Ong, Detection Technologies for Chemical Warfare Agents and Toxic Vapours, CRC Press 2005**

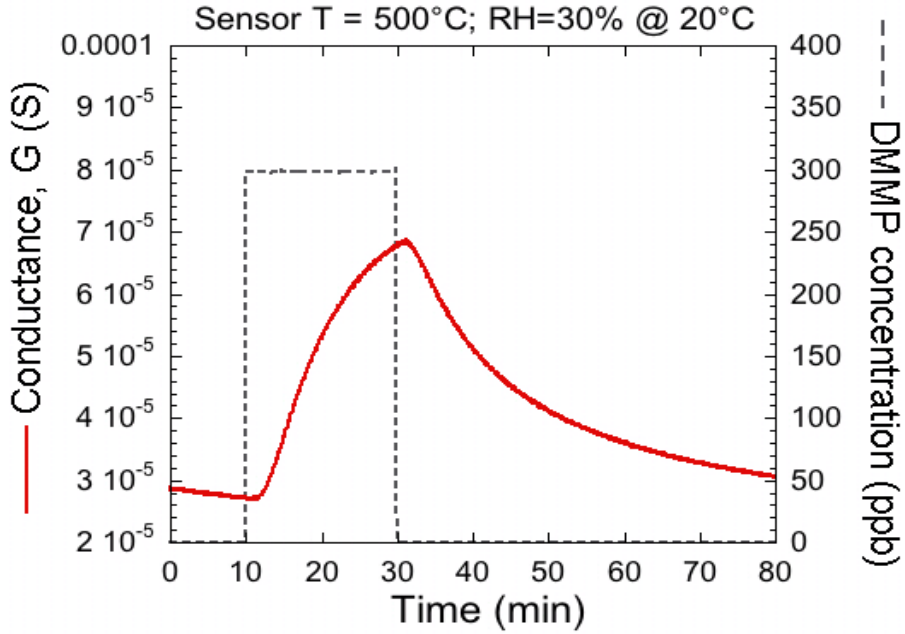
2. **PEL-TWA : Permitted Exposure Value - Time Weighted Average**

Sensitivity:

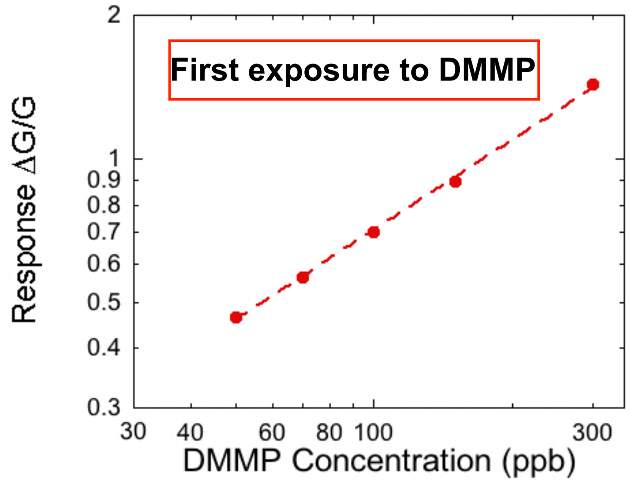
DMMP detection with SnO_2 NWs





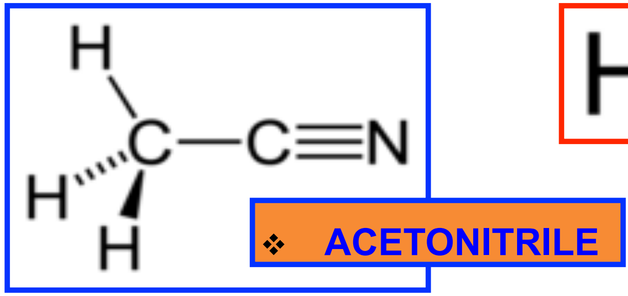


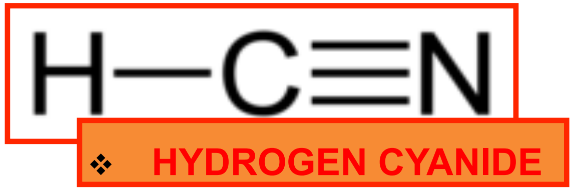
- DMMP: simulant for Sarin nerve agent
- DMMP adsorption leave P-O compounds over the metal oxide surface which are still present at 525°C, [1-3]
- Working T > 350°C to reduce poisoning effects
- Optimal working T=500°C
- SnO_2 NWs respond to DMMP at concentrations close to the Sarin IDLH value (0.03 ppm)



❖[1] C.S. Kim et al., Sens. Actuators B 76, 442 (2001)
❖[2] M.B. Mitchell et al., J.Phys. Chem. B 101, 11192-11203 (1997)
❖[3] A.A Tomchenko et al., Sens. Actuators B 108, 41-55 (2005)

Sensitivity:
Acetonitrile detection with SnO_2 NWs



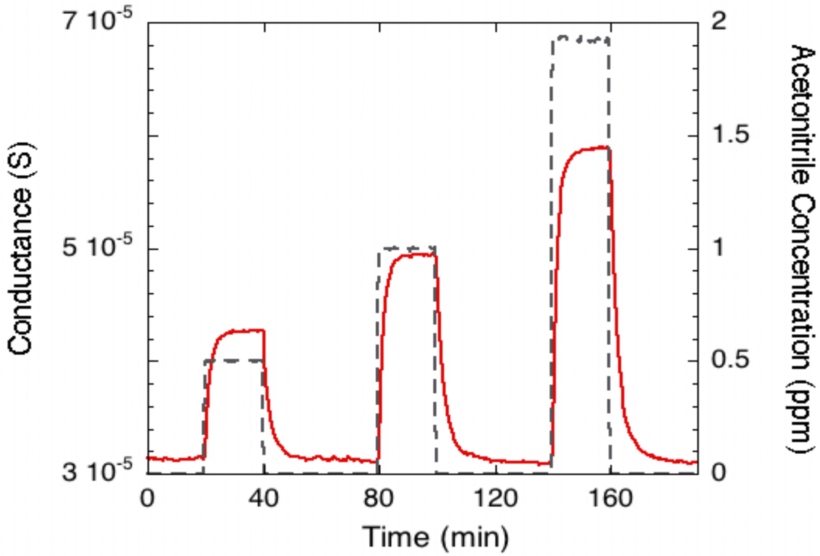


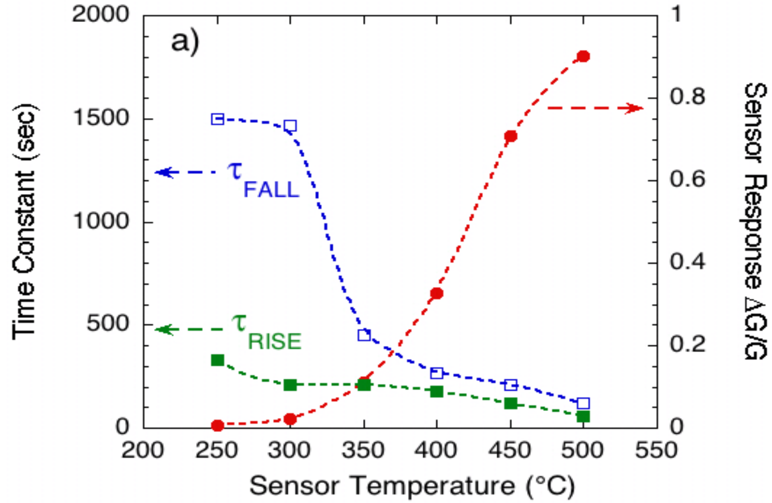
Acetonitrile (methyl cyanide): simulant for hydrogen cyanide;

Optimal working T = 500°C;

@500°C: Response (t_{RISE}) and recovery (t_{FALL}) times are comparable with chamber filling time (300 sec);

SnO_2 nanowires respond to acetonitrile at concentrations lower than the IDLH value (50 ppm)





A new device based on NWs technology and Surface Ionization phenomena.

SICS (Surface Ionization Chemical Sensors)

- Activity carried out in collaboration with Dr. G. Mueller (EADS (AIBUS) – Germany)

Surface Ionization (SI) phenomena

positive ions

$$\alpha = \frac{n_+}{n_0} = A_+ \exp\frac{q(\varphi - V_+)}{kT}$$

Degree of surface ionization α (ratio between the concentration of ionized and neutral ions) depends on the layer work function φ and on the molecule ionization potential (V_+) or electron affinity ($V\_$)

negative ions

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Molecule	qV_+ (eV)
Acetone	9.703
Ethanol	10.48
O_2	12.07
CO	14.01
NO_2	9.586

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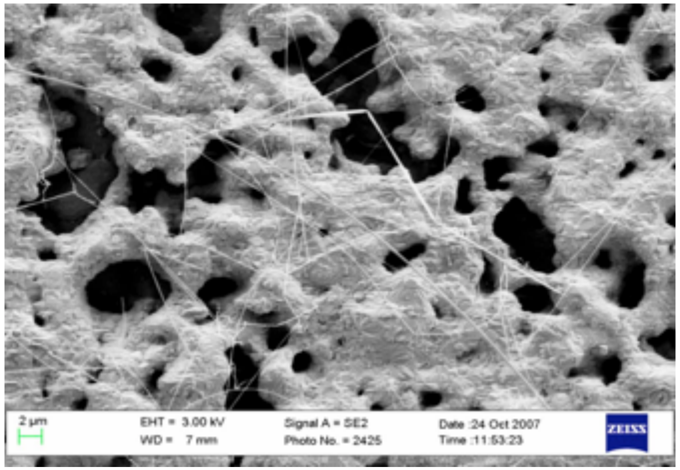
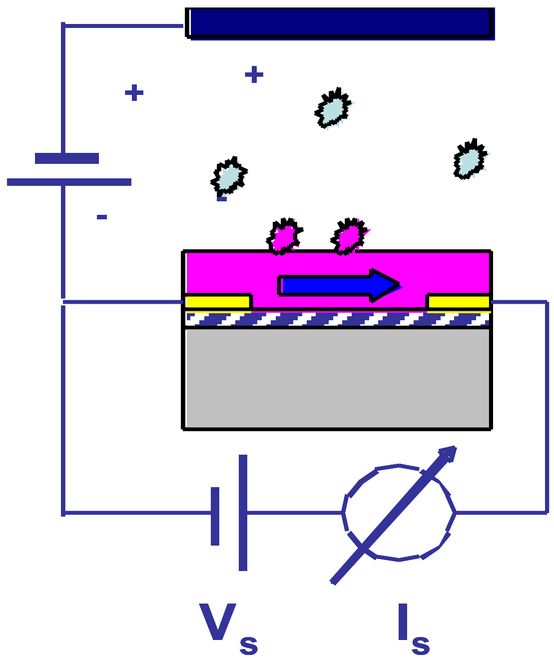
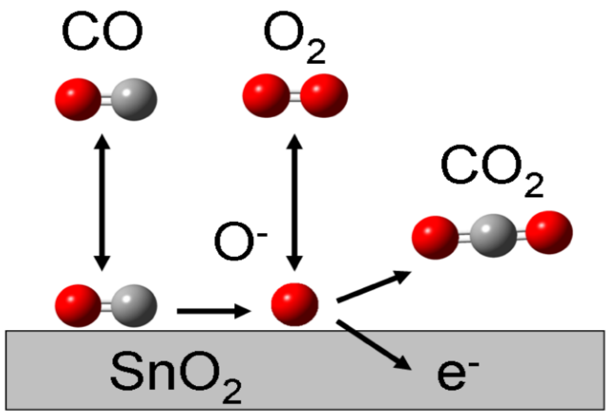
NANOWIRES

CAPABILITY OF HIGH ASPECT RATIO NANOSTRUCTURES TO CONCENTRATE HIGH ELECTRIC FIELDS AT THEIR APEX



U.K Rasulev , E.Y. Zandberg; Progr.Surf.Sci.28 (1988)

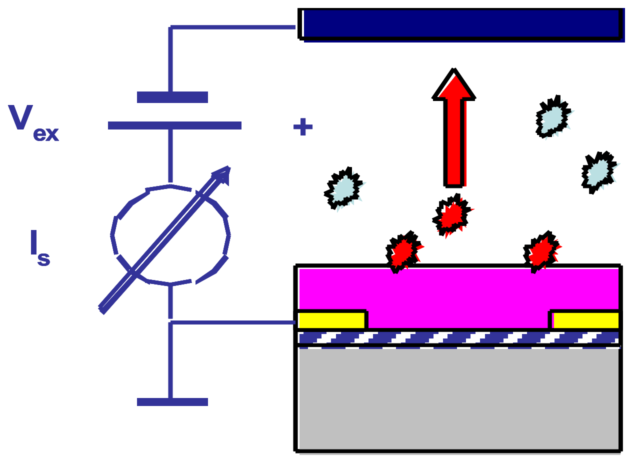


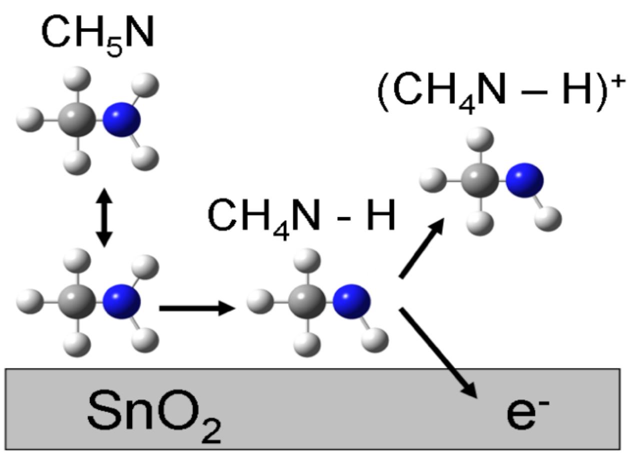


Resistive (RES) response:

Adsorbed analytes (CO) suffer electrically detectable combustion reactions by reacting with co-adsorbed surface oxygen ion species

Detection criterion: combustibility → poor selectivity



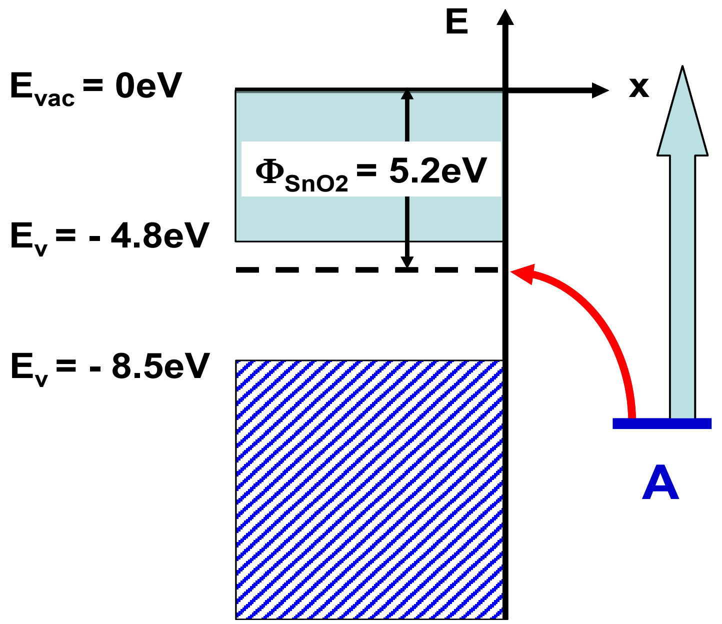


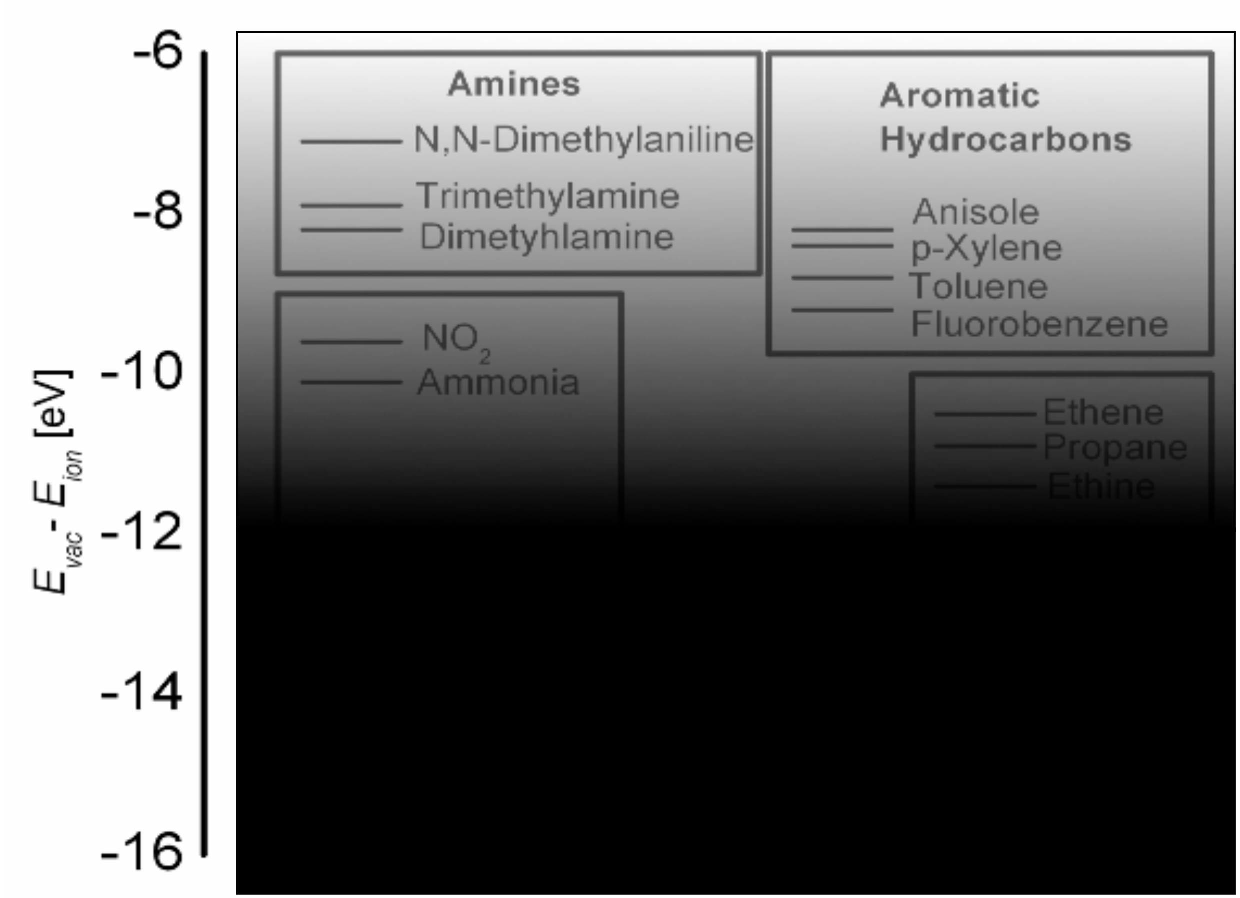
Surface ionisation (SI) response:

Valence electrons are transferred to empty electron states inside adsorbent solid.

Detection criterion: Ionisation energy

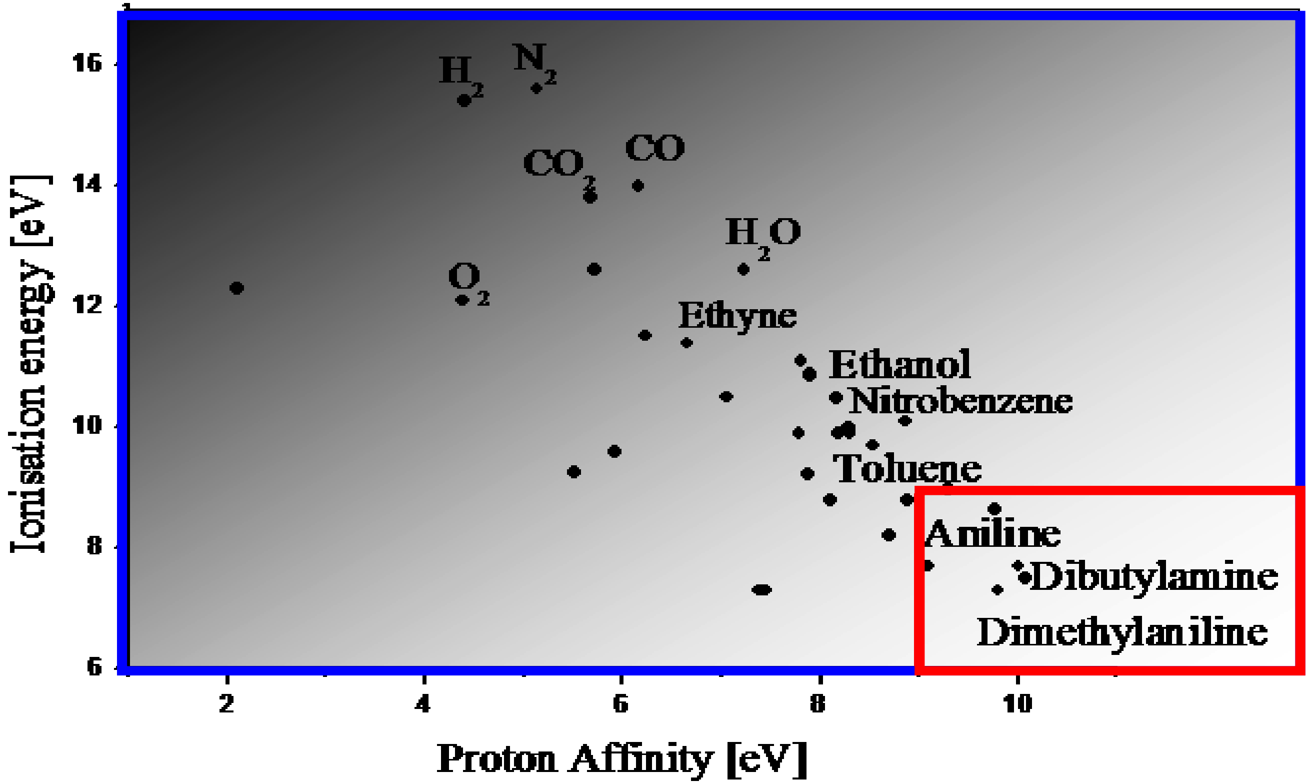
→ Selectivity towards higher interest analytes





SI detection is blind against high ionisation energy analytes

→ Selectivity against toxic, odorous, reactive analytes !



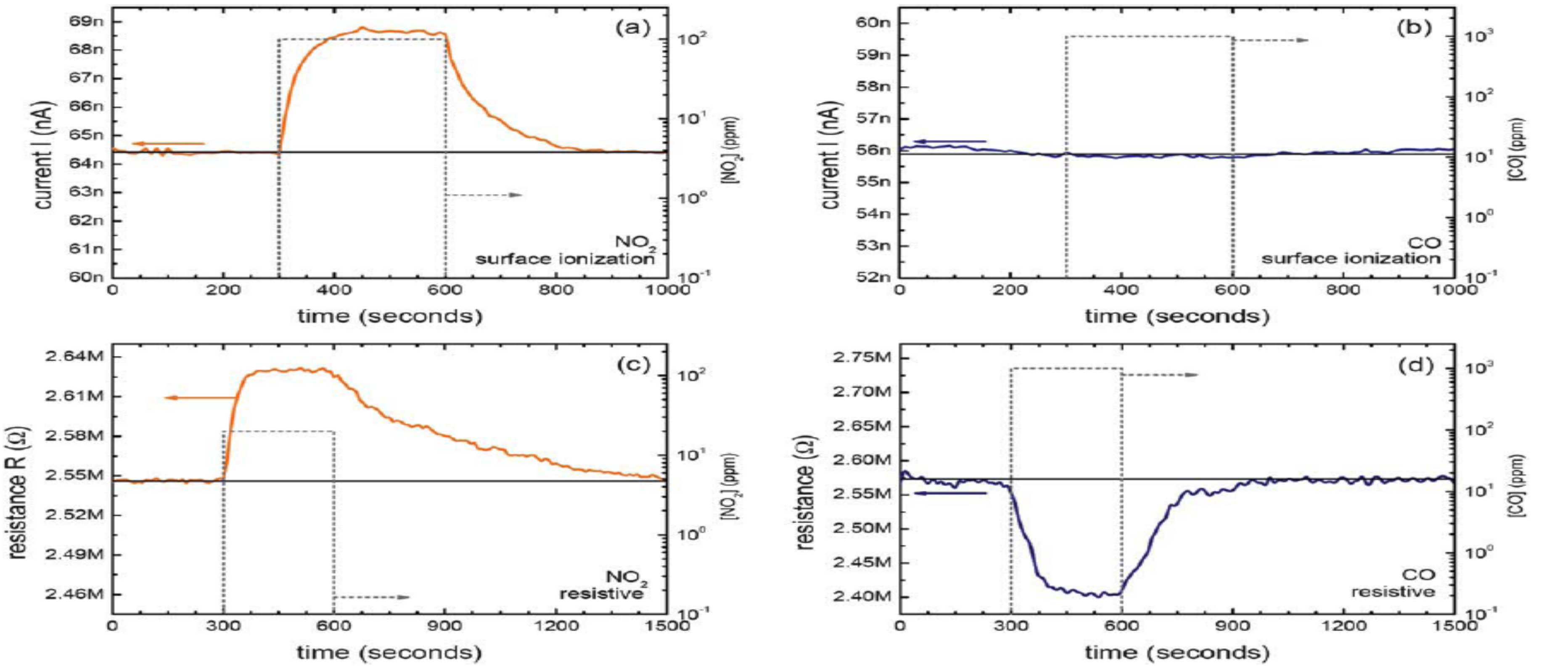
RESistive Response

Surface Ionisation Response

RES detection: All kinds of hydrocarbons (HC)

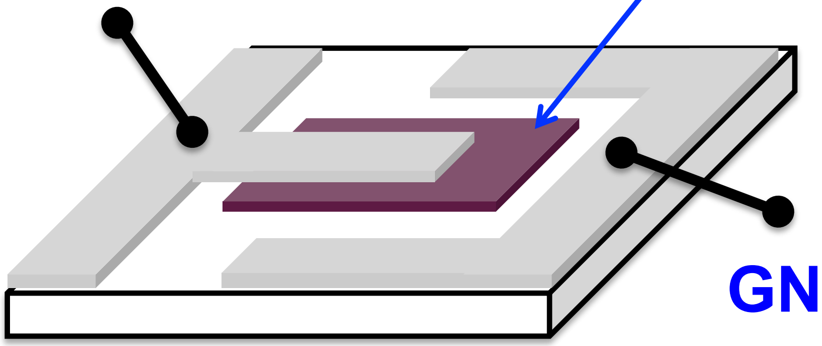
SI detection: HC with amine functional groups (smelly and toxic)

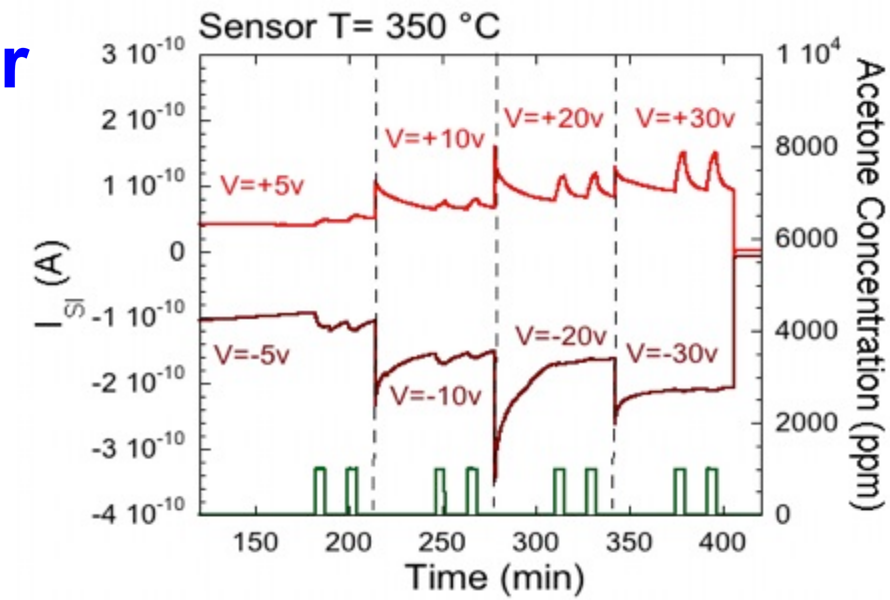
Combination of SI and RES response to address selectivity with ZnO NWs.



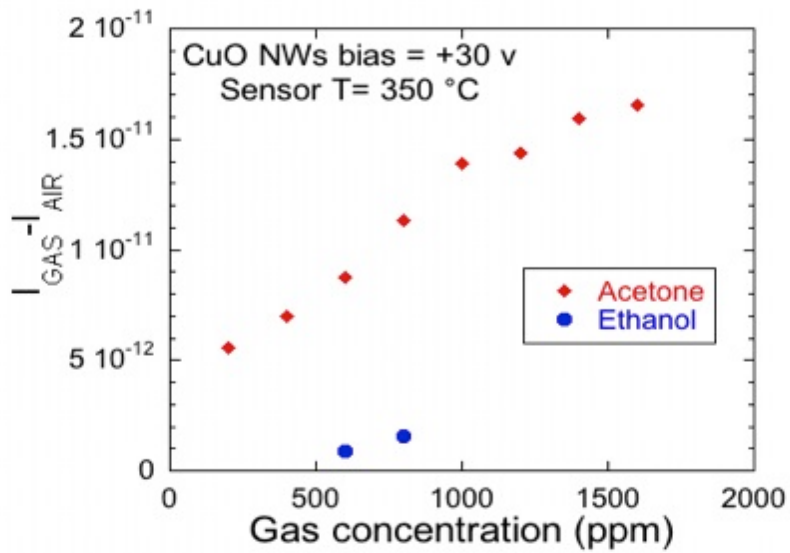
- **Work in progress: Preparation of the single device featuring multiparametric readout**

Surface ionization (SI) - horizontal layout





- •Only CuO positively biased shows response to gases;
- • Response to ethanol is much lower than the response to acetone (in agreement with first ionization energy values);
- •SI response measured at much lower electric field (150 V/cm) with respect to the vertical layout



SENSOR

Conclusions

- The fundamental properties of nanosized materials have been studied over the last years with particular focus on the possibility to exploit the preparation of **new devices such as SICS (Surface Ionization Chemical Sensors)**
- A great effort has been done to **understand** and **control** the **growth process** for the production of high quality quasi one-dimensional nanostructures with bottom up techniques and their integration in functional devices.
- Different ways to **exploit** NWs peculiarities have been proposed to obtain chemical sensors for explosive and toxic gases.

Giorgio Sberveglieri

Thank to the SENSOR Lab members!

http://sensor.ing.unibs.it

Thank you for your attention !

EUROPEAN COOPERATION IN SCIENCE AND TECHNOLOGY