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

COST Action TD1105

INTERNATIONAL WG1-WG4 MEETING on

New Sensing Technologies and Methods for Air-Pollution Monitoring

European Environment Agency - EEA

Copenhagen, Denmark, 3 - 4 October 2013

Action Start date: 01/07/2012 - Action End date: 30/06/2016 - Year 2: 2013-2014 (*Ongoing Action*)

Low-Cost Metal Oxides Gas Sensors: State of Art, Perspectives and New Challenges

(New nanomaterials and processes for fully integrated all-solid state reliable gas sensor on micro machined platforms: conductometric, surface ionization and electrochemical sensor types)

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IREC Catalonian Institute for Energy Research
Barcelona, Spain

COST is supported by the EU Framework Programme

ESF provides the COST Office through a European Commission contract

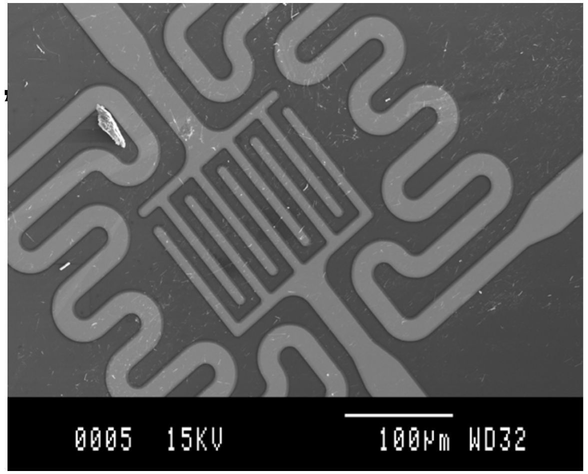
Scientific context and objectives

- **Background / Problem statement:**

Since 1962 it has been known that metal oxide thin films interact with gaseous components from the surrounding ambient [1]. “A new detector for gaseous components using semiconductor thin films”

The main consequence of this interaction is modification of their electrical characteristics and, consequently, it can be used as the basis for gas detector development. A great deal of effort has been made to improve the knowledge and understanding of the related processes.

During the last 50 years many critical issues related with the sensing phenomena and performances have been analyzed and studied and it is corresponding to the history of solid state metal oxide based gas sensors:



the interaction of the metal oxide surface with oxygen and water [2],
the effects of the additives [3],
the role played for catalysts [4, 5],
the significance of the grain size [6],
the modeling of the sensor response laws [7, 8], etc

[1] Seiyama T, Kato A, Fujiishi K and Nagatani M 1962 Anal. Chem. 34 1502
[2] Yamazoe N, Fuchigami J, Kishikawa M and Seiyama T 1979 Surf. Sci. 86 335
[3] Yamazoe N, Kurokawa Y and Seiyama T 1983 Sensors Actuators B 4 283
[4] Iwamoto M, Yoda Y, Egashira M and Seiyama T 1976 J. Phys. Chem. 80 1989
[5] Seiyama T, Yamazoe N and Eguchi K 1985 Indust. Eng.Chem. Prod. Res. Dev. 24 19
[6] Xu C N, Tamaki J, Miura N and Yamazoe N 1991 Sensors Actuators B 3 147
[7] Yamazoe N and Shimanoe K 2008 Sensors Actuators B 128 566
[8] Yamazoe N and Shimanoe K 2011 Sensors Actuators B 158 28

cost EUROPEAN COOPERATION IN SCIENCE AND TECHNOLOGY

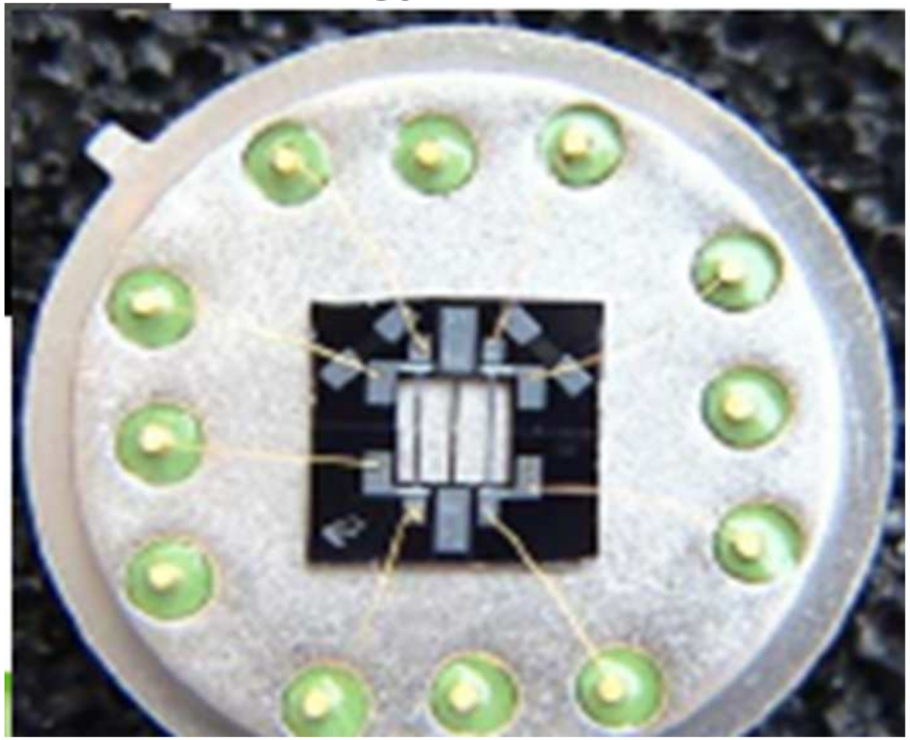
IREC Institut de Recerca en Energia de Catalunya
Catalonia Institute for Energy Research

Scientific context and objectives

- **Background / Problem statement:**

Nevertheless, in spite of the growing commercial success [9–15], keeping low cost, many basic issues still remain open and under discussion, limiting the broad use of this technology.

[9] www.figarosensor.com/
[10] www.fisinc.co.jp/
[11] www.alphasense.com/
[12] www.alpha-mos.com/
[13] www.appliedsensor.com/
[14] www.e2v.com/
[15] www.umweltsensortechnik.de/



Scientific context and objectives

- **Background / Problem statement:**

Commercial solid state gas sensors are currently based on thin/thick layers or micro bead of metal oxide semiconductors deposited onto heaters platform, which are used to control the temperature at the optimal values to activate the surface transduction mechanisms.

TH (H)	Heating time (high)	5 sec ± 0.1 sec	
TH (L)	Heating time (low)	20 sec ± 0.1 sec	
I_S (H)	Current consumption (high)	132mA ± 15mA	VH=0.9V
I_S (L)	Current consumption (low)	59mA ± 10mA	VH=0.2V
Ps	Power dissipation	Less than 10 mW	

Heater voltage cycle	V_H	V_{HH}=4.8V±0.2V DC, 14ms V_{HL}=0.0, 986ms
Circuit voltage cycle	V_C	V_C=0V for 995ms, V_C=5.0V±0.2V DC for 5ms
Load resistance	R_L	variable (≥10kΩ)
Heater resistance	R_H	17 ± 2.5Ω at room temp.
Heater current	I_H	approx. 203mA(in case of V_{HH})
Heater power consumption	P_H	approx. 14mW (ave.)

Heater Voltage	V_H	V_{HH} = 0.9V±3%, 5 sec. V_{HL} = 0.2V±3%, 15 sec.	
Circuit voltage	V_C	5.0±0.2V DC pulse *(refer to Technical Information for TGS3870)*	
Load resistance	R_L	Variable (>0.75kΩ)	
Heater resistance	R_H	3±0.3Ω at room temp.	
Heater power consumption	P_H	120mW	V_{HH} = 0.9V DC
		11mW	V_{HL} = 0.2V DC
		38mW	average

Scientific context and objectives

- **Background / Problem statement: Reliable for large market but expensive**

» Home
» Company Profile
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» Products
- Carbon Dioxide Sensors
- NDIR Sensors
- Carbon Monoxide B4
- Hydrogen Sulfide B4
- Nitric Oxide B4
- Nitrogen Dioxide B4
- Sulfur Dioxide B4
- Ozone B4
- Optical Particle Counter
- PID Sensors
- Integrated Sensor Boards

» Downloads
» Links
» Industrial

Carbon Monoxide 4-Electrode Sensor

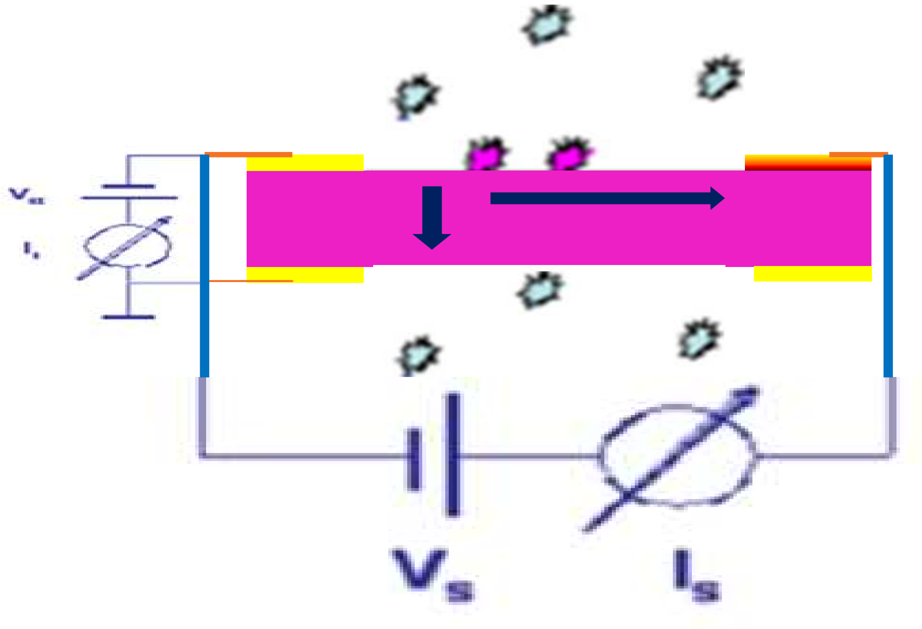
Alphasense 4-Electrode gas sensors operate using proven fuel cell technology.

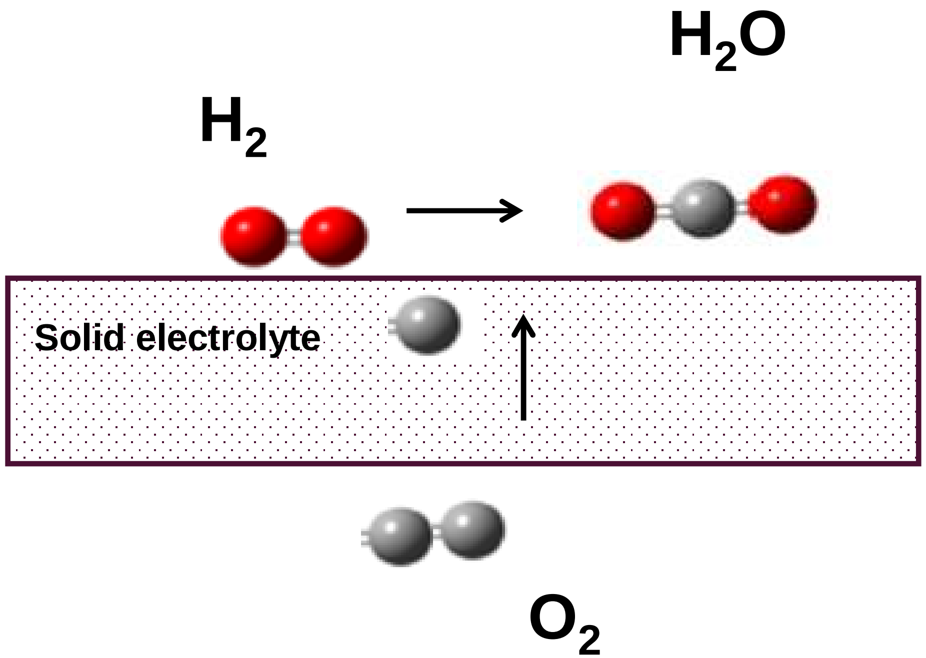
The B4 series (4-electrode sensors) provides OEMs with reliable sensors for use in a number of high volume applications and especially Air Quality Networks where very low parts per billion (ppb) detection levels are required. Strong signal levels combined with low zero current allows resolution to < 10 (ppb) and a wide operating range. The sensors are suitable for use in fixed installation sensing heads, portable safety instruments, urban/indoor air monitoring and stack gas analysers.

The B4 series of sensors offer our electrolyte leak-free guarantee and reliable long-term detection performance. The leak-proof housing is moulded with a colour coded top for ease of identification.

Alphasense tests the performance of every sensor; results are stored on our database, giving full traceability for all sensors. The unique Automatic Test and Validation (ATAV) system controls initial sensor stabilisation and runs complex tests under computer control. This computerised system also ensures traceability as tested sensors are moved direct to despatch with their unique barcodes. The ATAV system also

Electrical response (I or V) due to the electrochemistry processes

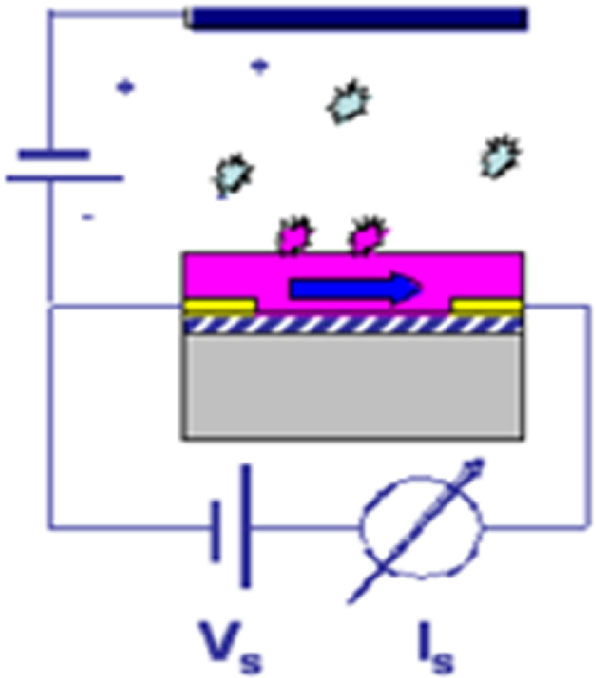


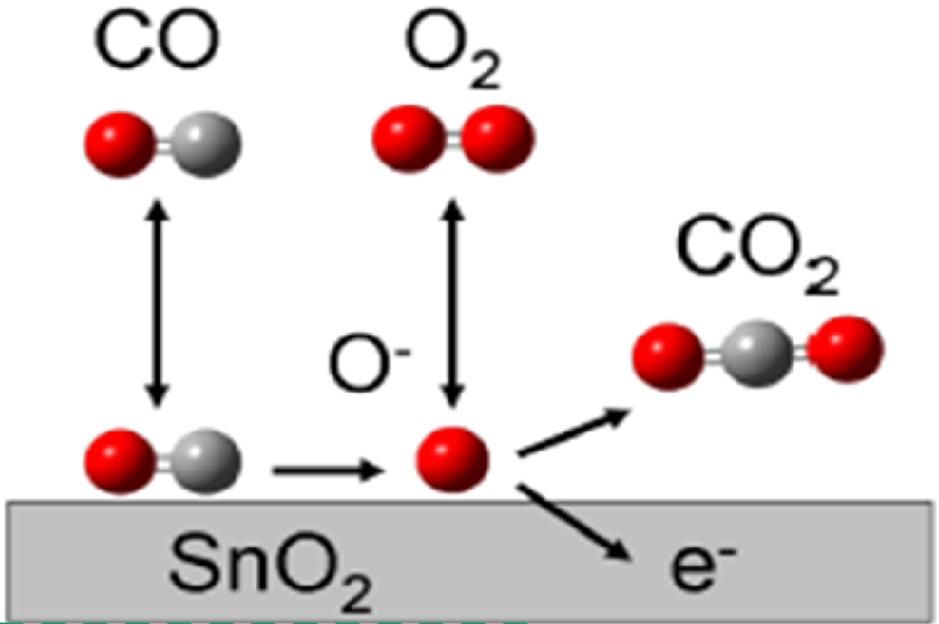


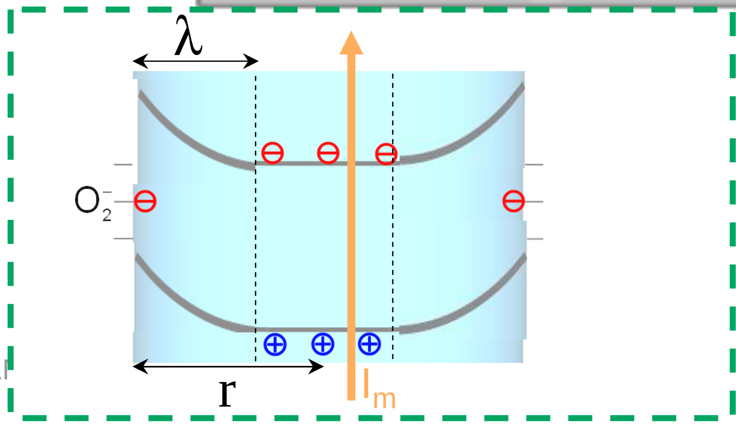
Scientific context and objectives

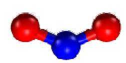
- **Brief reminder of objectives:**

Resistive response due to the surface modifications









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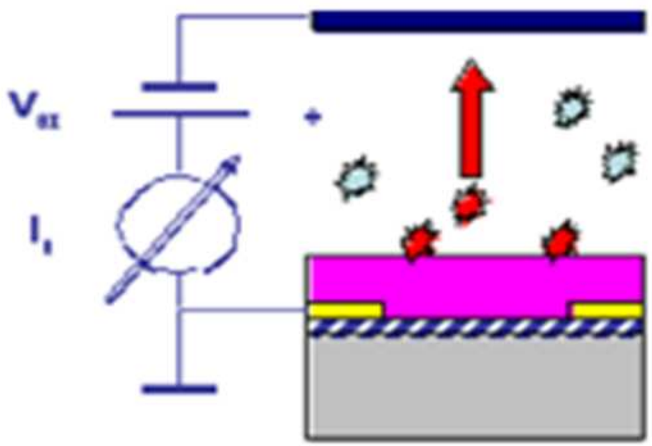
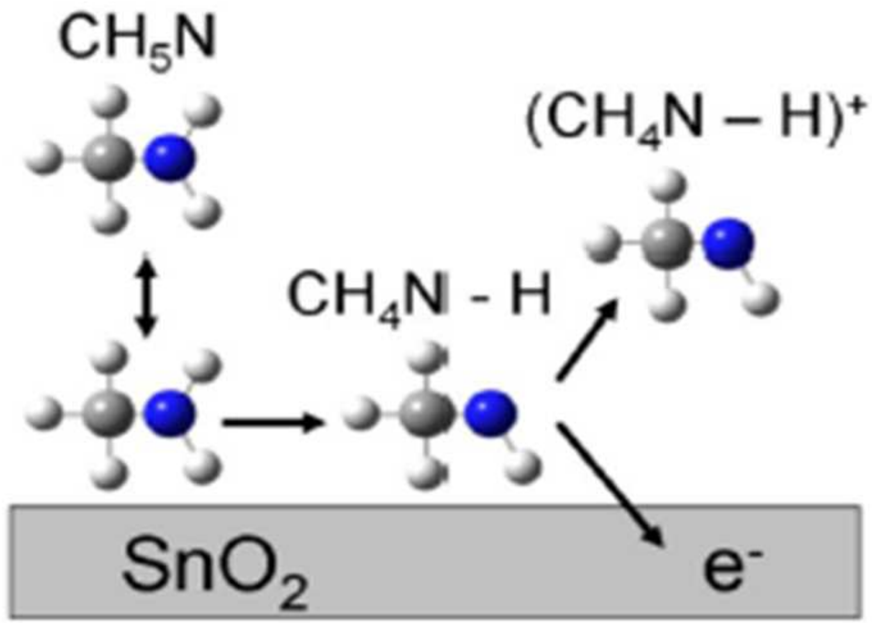
Scientific context and objectives

- **Brief reminder of objectives:**

Ionization response due to the <u>surface ionization</u> processes

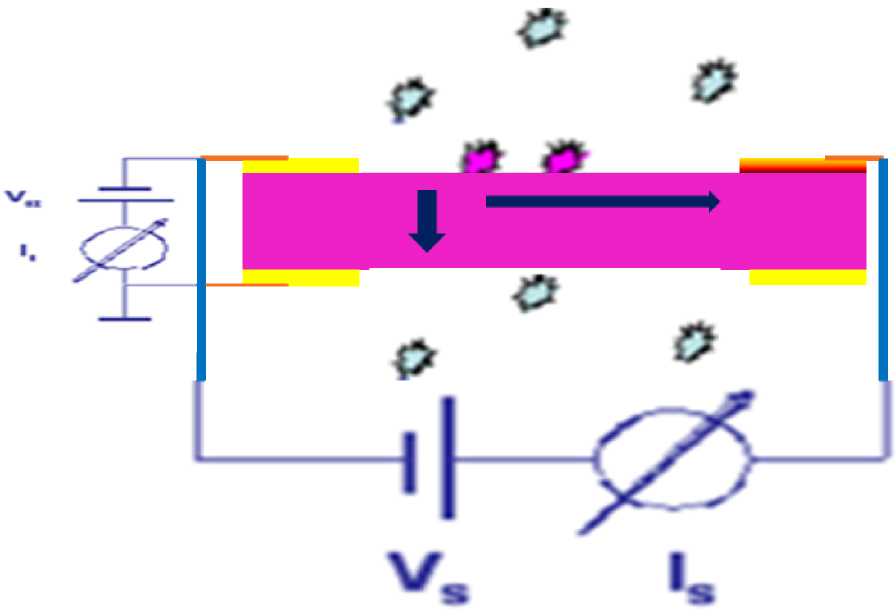


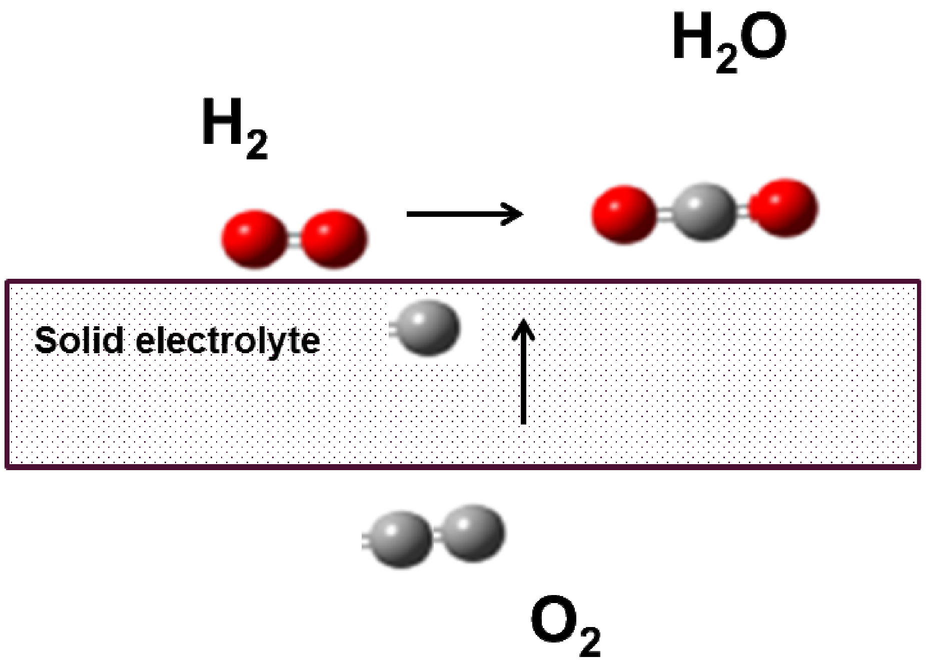


Scientific context and objectives

- **Brief reminder of objectives:**

Electrical response (I or V) due to the electrochemistry processes





FULLY INTEGRATED
ALL-SOLID-STATE SENSORS
ON MICROMACHINED PLATFORMS:
NEW TYPE OF GAS SENSORS
Resistive sensor based on Nanostructures

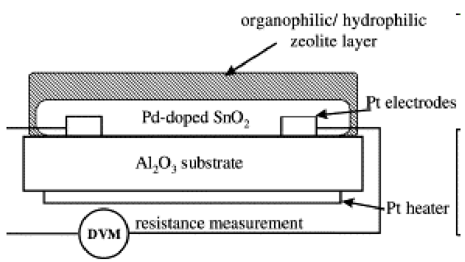
Scientific context and objectives

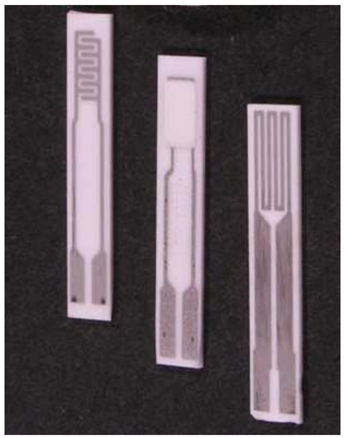
- **Brief reminder of objectives:**

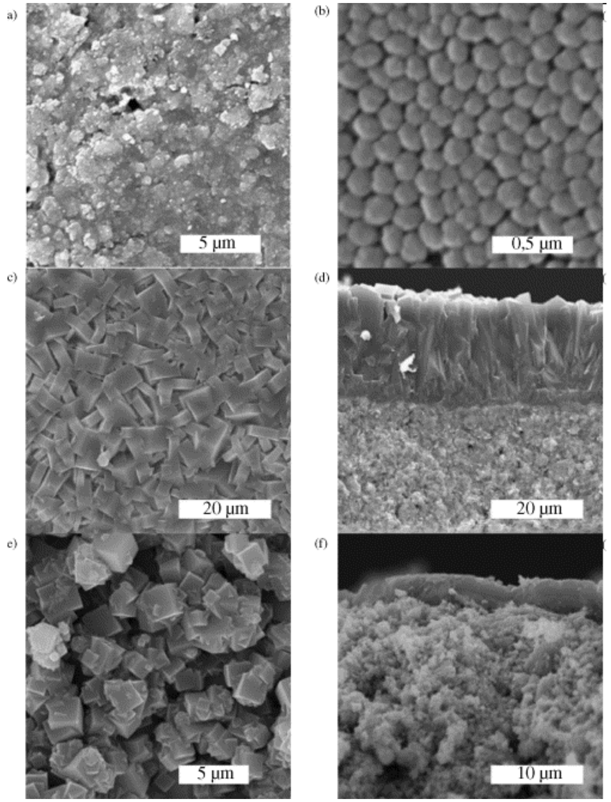
sensing platforms

Alumina substrates

SNB **31**, 1 (1996)
J. Appl. Phys. **90**, 1550 (2001)
Catal. Today **82**, 179(2003)



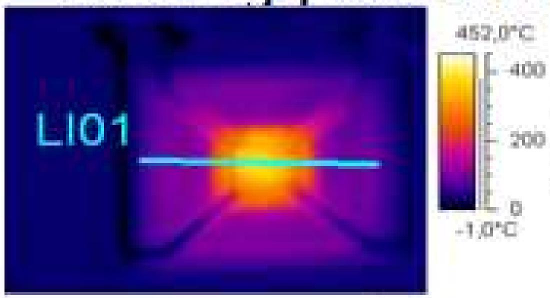


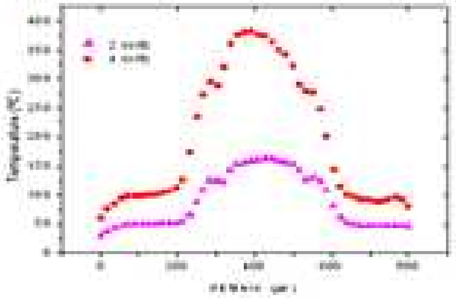


Scientific context and objectives

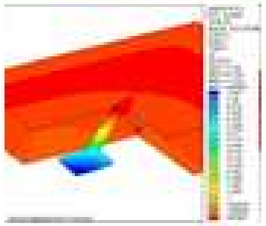
- **Brief reminder of objectives:**

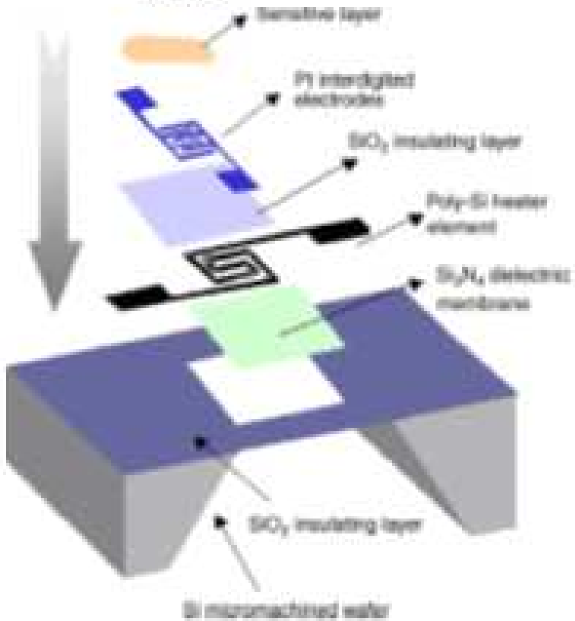
sensing platforms

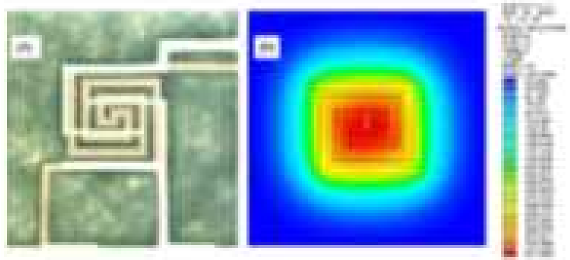


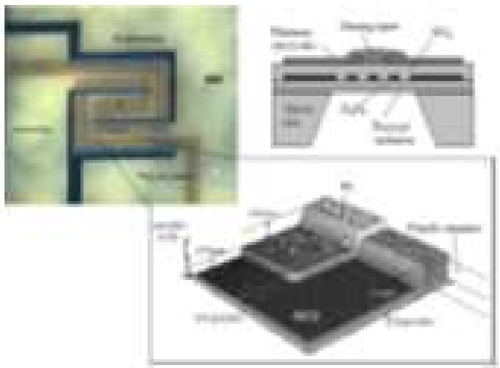


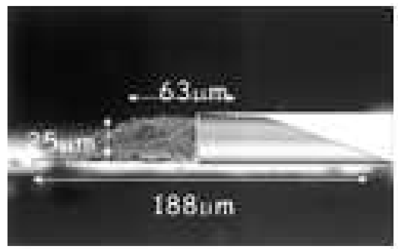
SNB 84, 60 (2002)
SNB 95, 275 (2003)
J. Micromech. Microeng. 13, S119 (2003)
J. Micromech. Microeng. 13, 548 (2003)
SNB 114, 826 (2006)
SNB 114, 881 (2006)



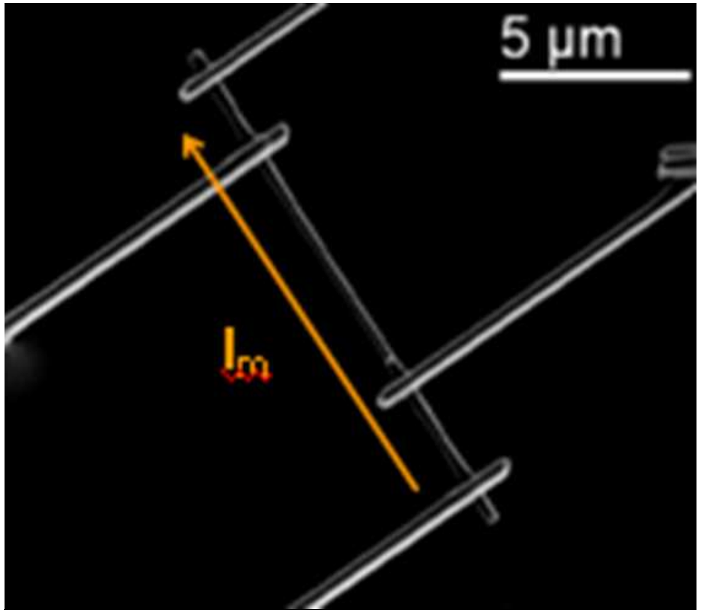


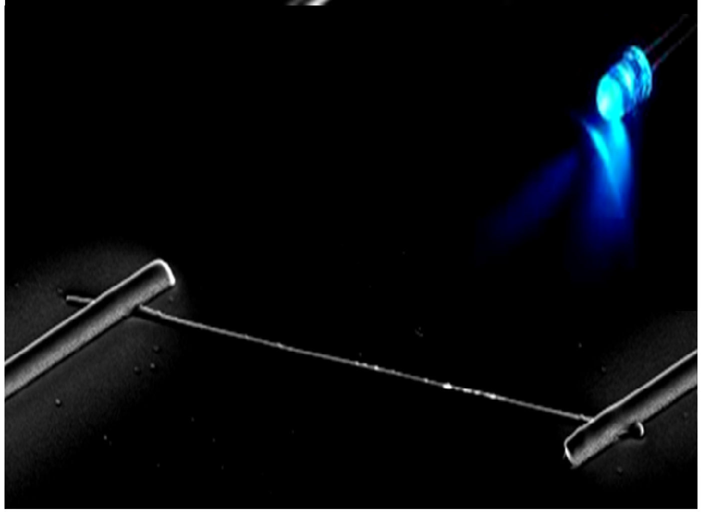




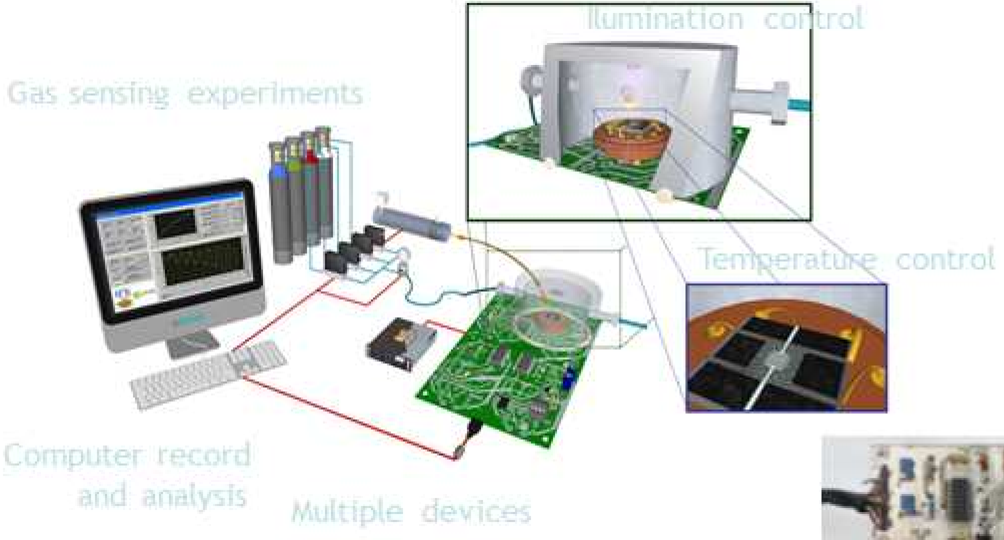


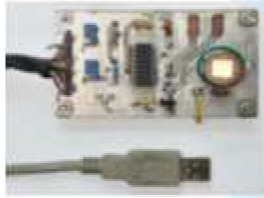
Sensing platforms based on **individual nanowires**

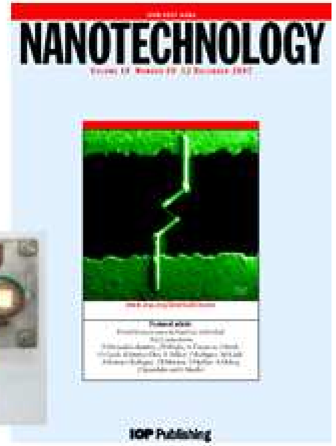




Electrical characterization



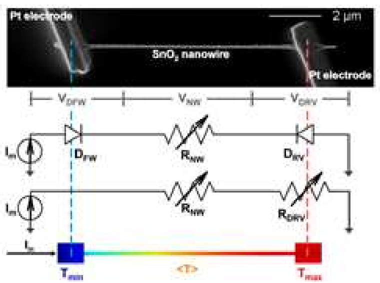


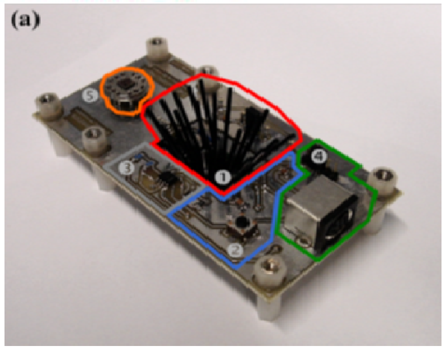


Nanotechnology 18, 495501 (2007)
mst/news 3/08, 6 (2008)

"very low power consumption: less than 20µW (and even less)"
(measurement AND HEATING included!!!)

APL (2008)





J of PhysChem C (2008)
APL,(2009)
S&A:B (2010,2011)

cost
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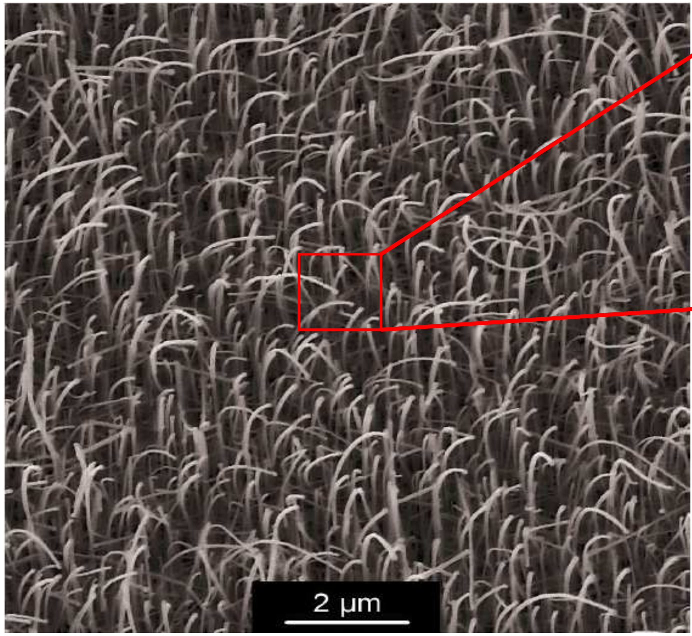
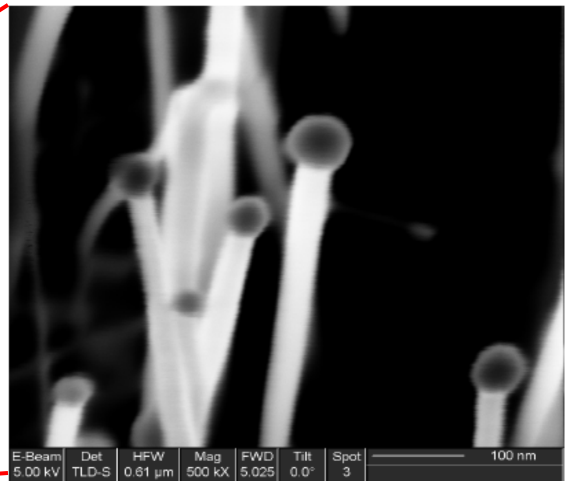
Using individual nanowire as experimental platform

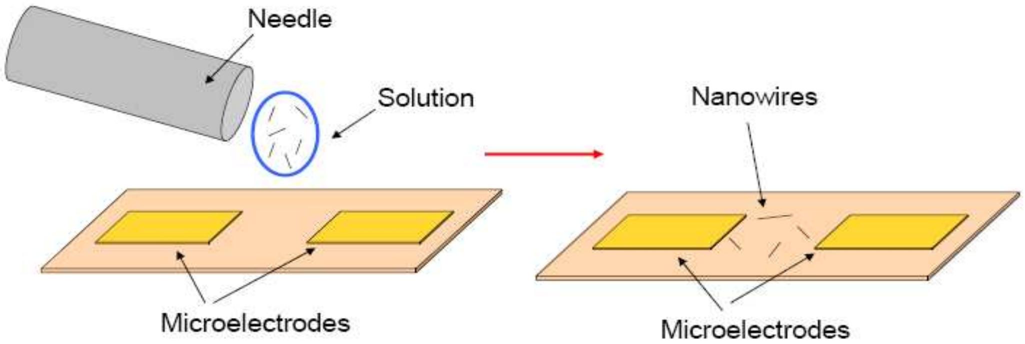
Nanowires are dispersed over a substrate with pre-patterned microelectrodes:

Adv. Funct. Mater. 10.1002/adfm.200701191



SnO_2 Nanowires





Individual nanowire platforms

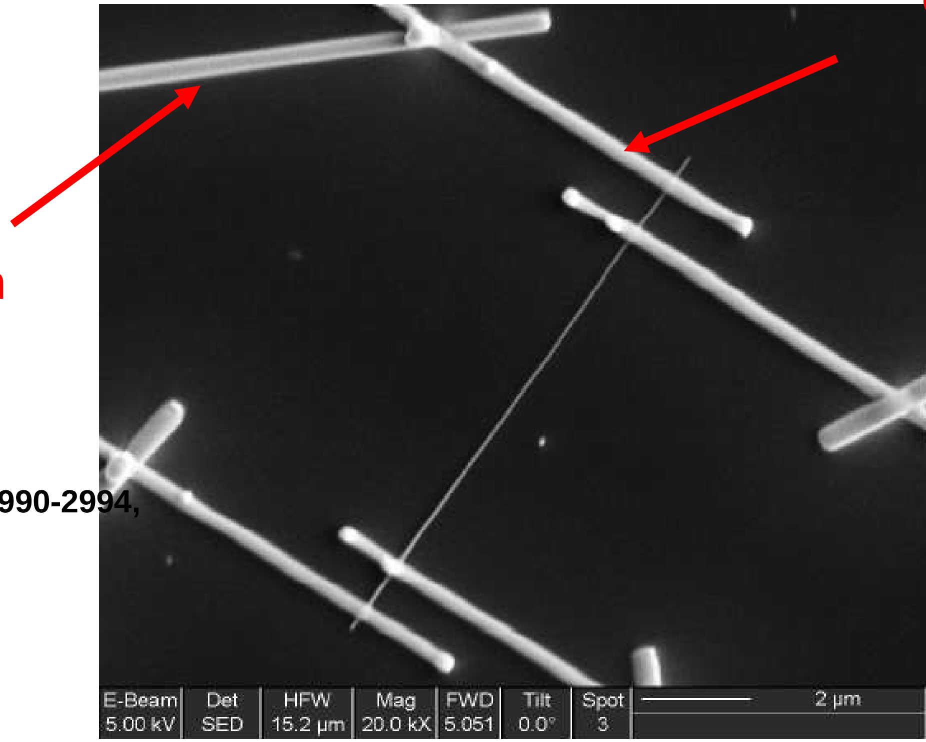
Nanofabrication: botom-up approach

- ✓ **Immediate test of novel materials**
- ✓ **Nanowires contacted with e^- & i^- beam FIB nanolithogaphy**

***Nanotechnology* 17, 5577 (2006)**

e-beam

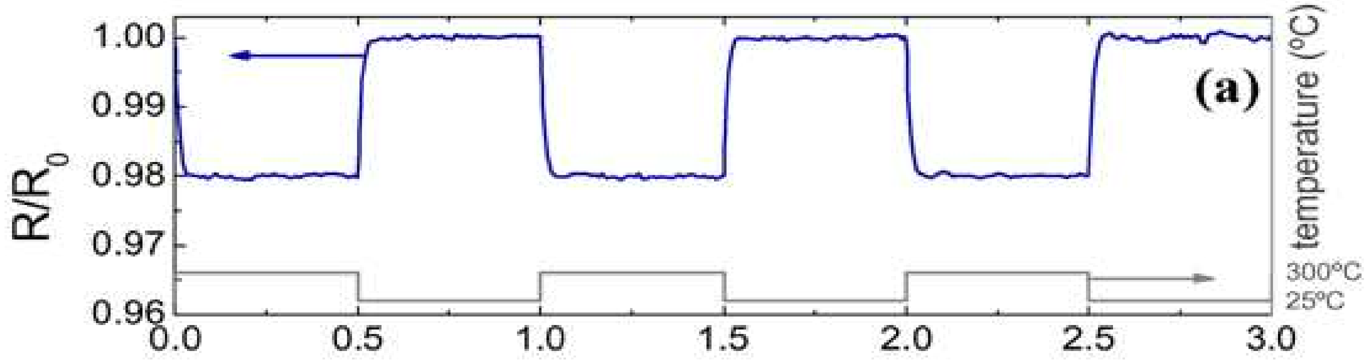
i-beam

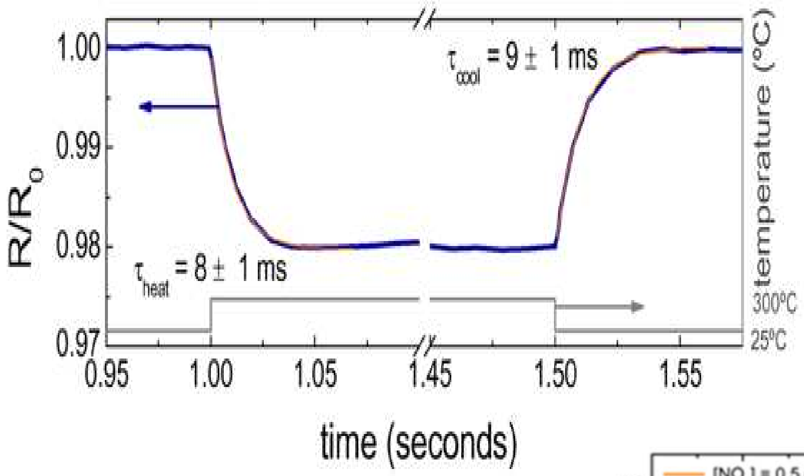


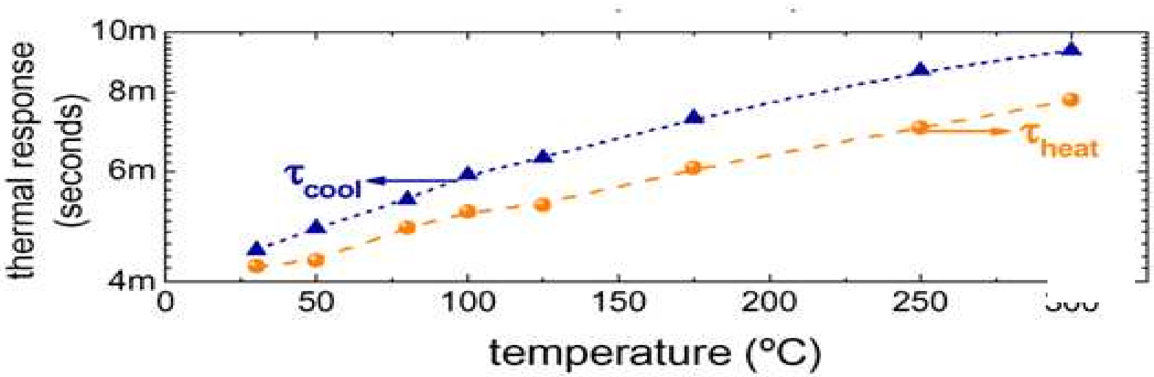
Nanotechnology, 18(49) 2007

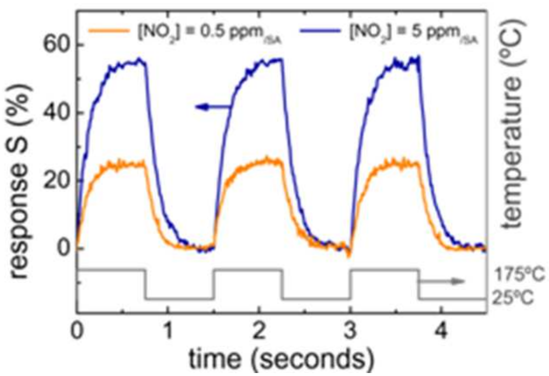
Advanced Functional Materials 18,2990-2994, (2008)

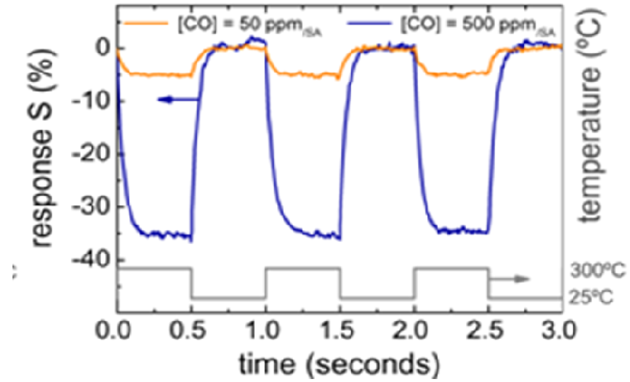
Thermal inertia: thermal time constants versus chemical reactions at the Mox surface







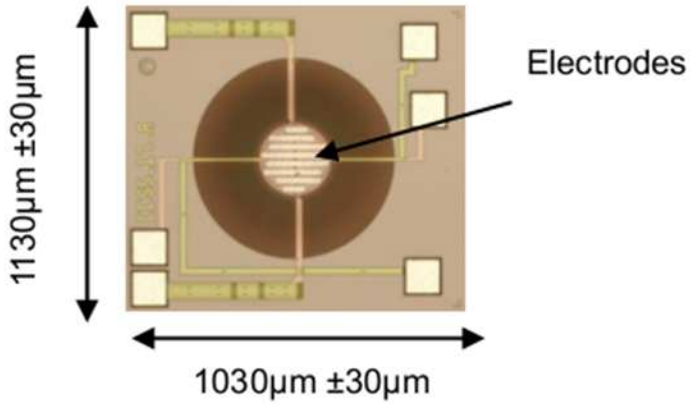


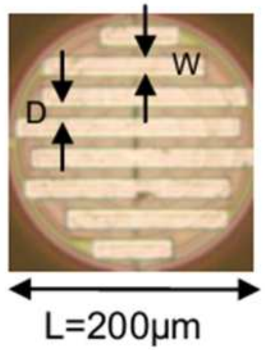


Scientific context and objectives

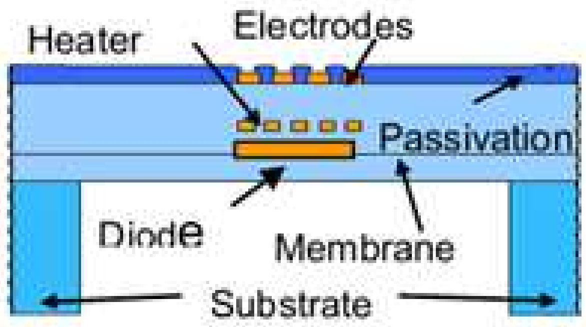
- **Brief reminder of objectives: new performance hotplate for improved gas sensors based on SOI technology**

Die Dimension	Electrode Dimension



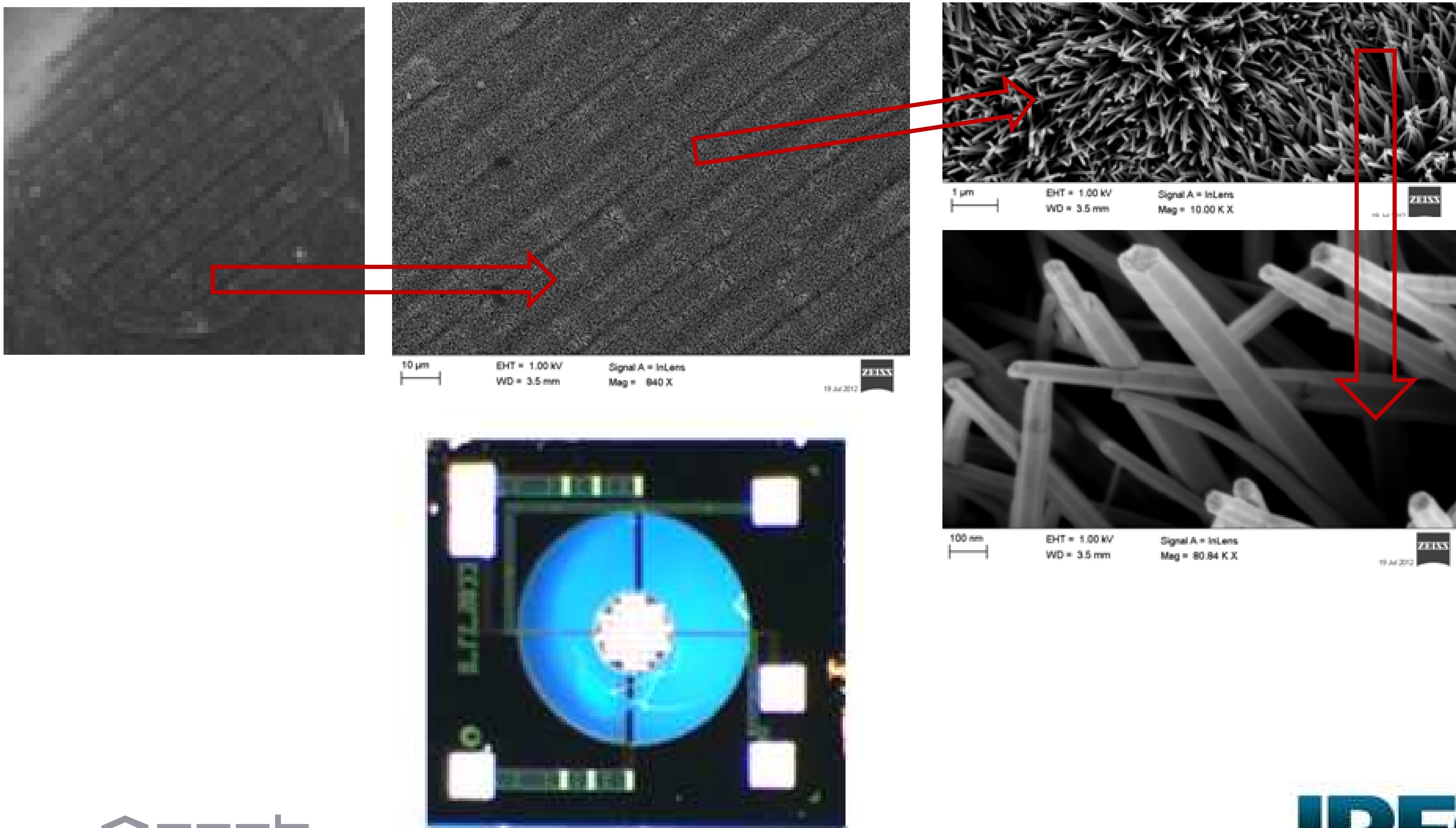


IDE Width (W): ~18µm
Separation (D): ~8µm
Electrodes: 2 x 4
Aspect Ratio: ~120

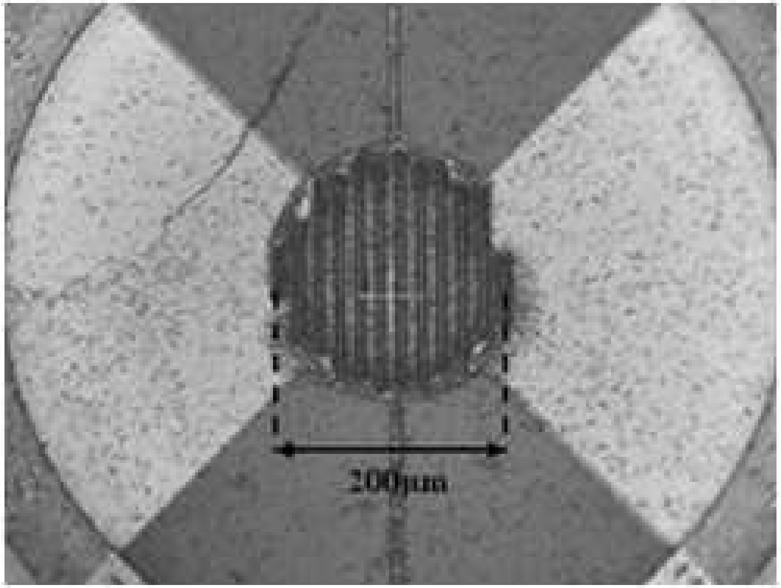


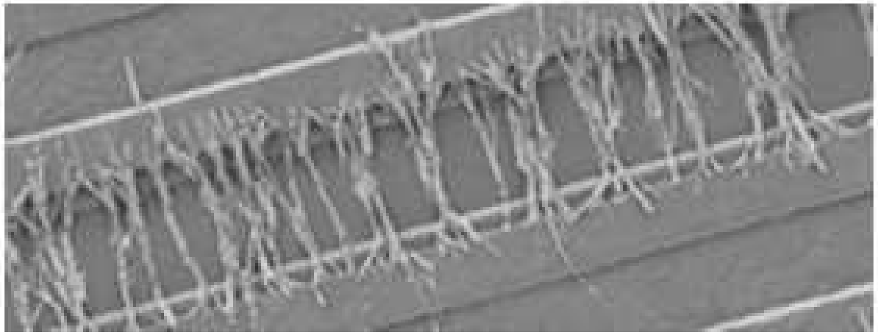
7fp ICT:SOI-HIT

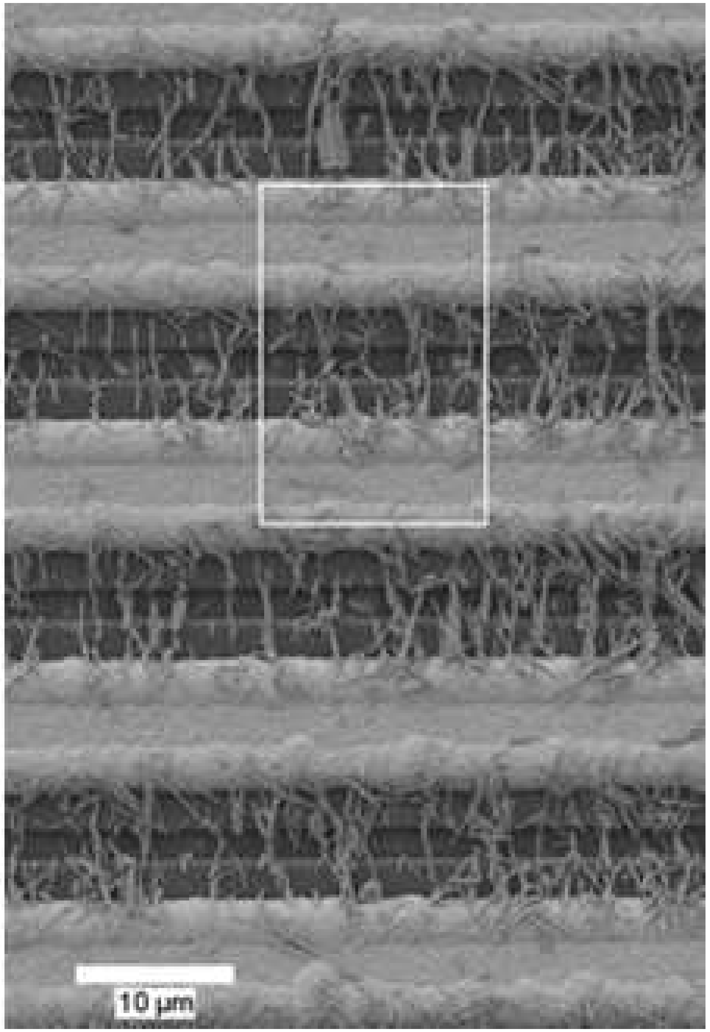
New materials and processes



New materials and processes

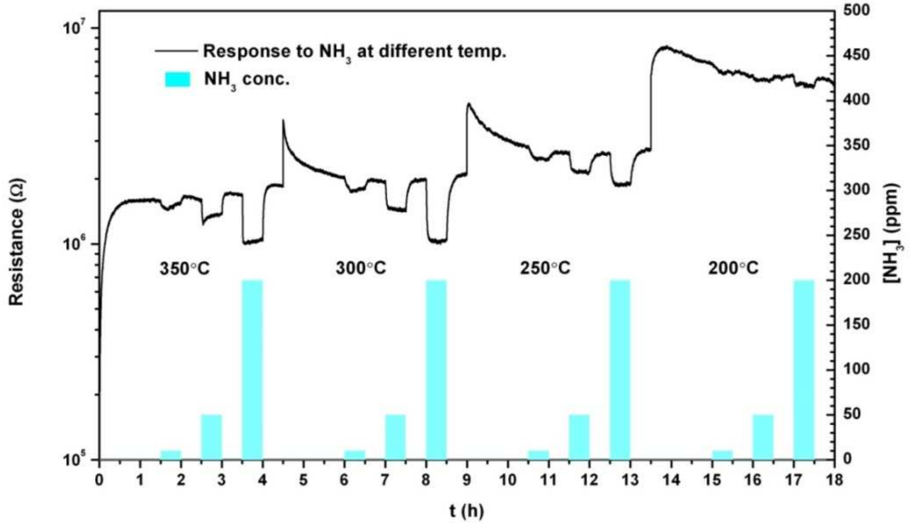




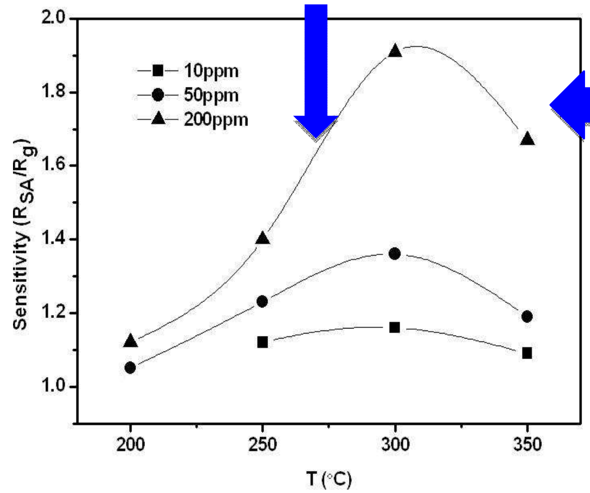


New materials and processes

Isothermal mode

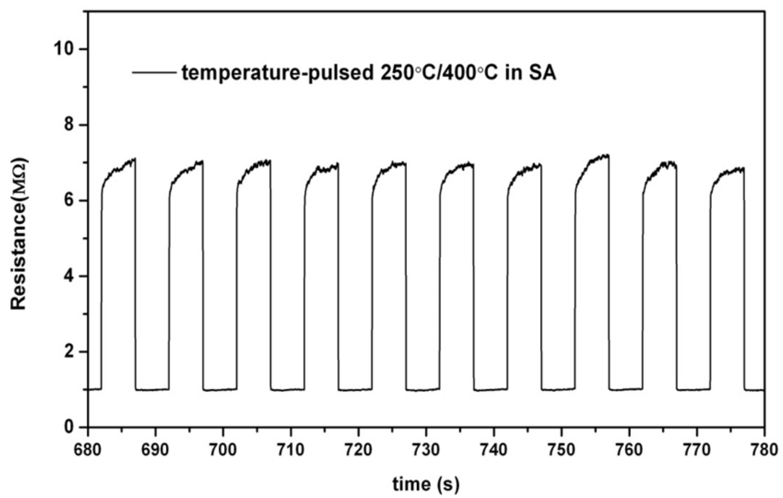


Surface reactivity



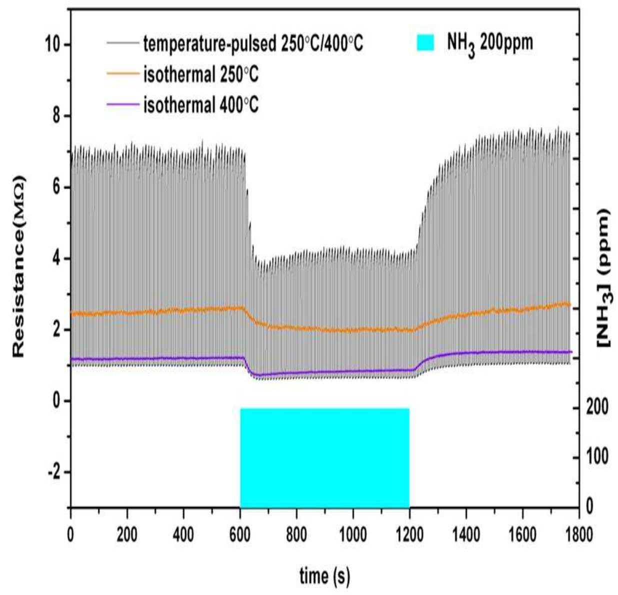
Surface desorption

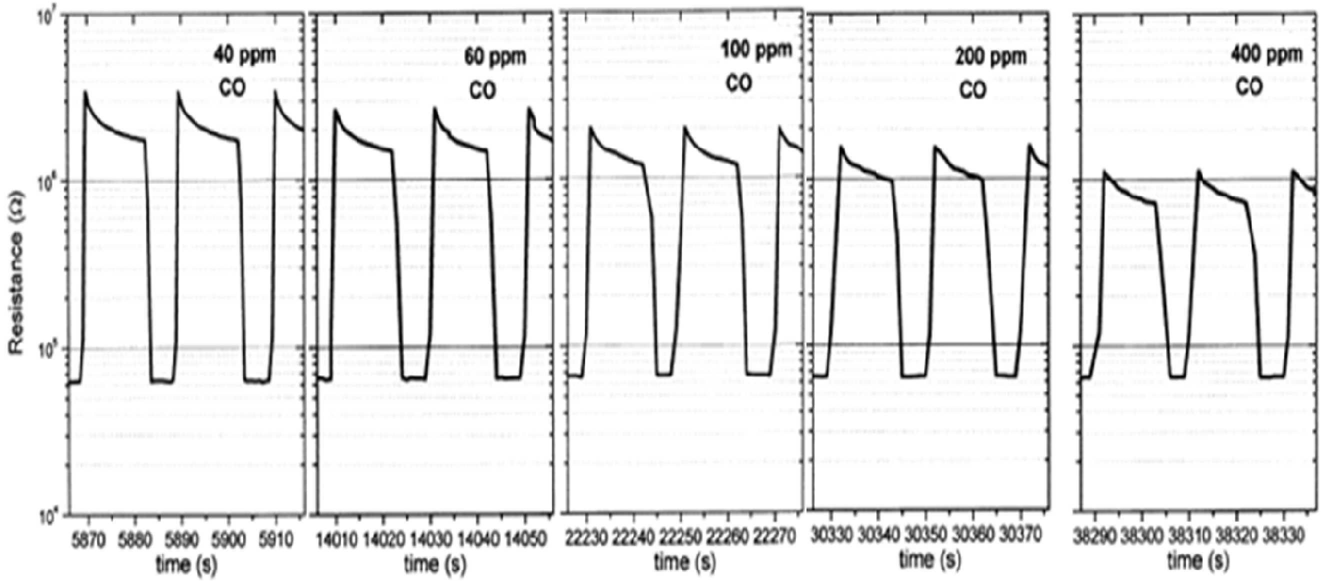
Pulsed mode



New materials and processes

Improving sensing due to the pulsed mode: stimulating sensing surface at high temperature and freezing sensing conditions at low temperature

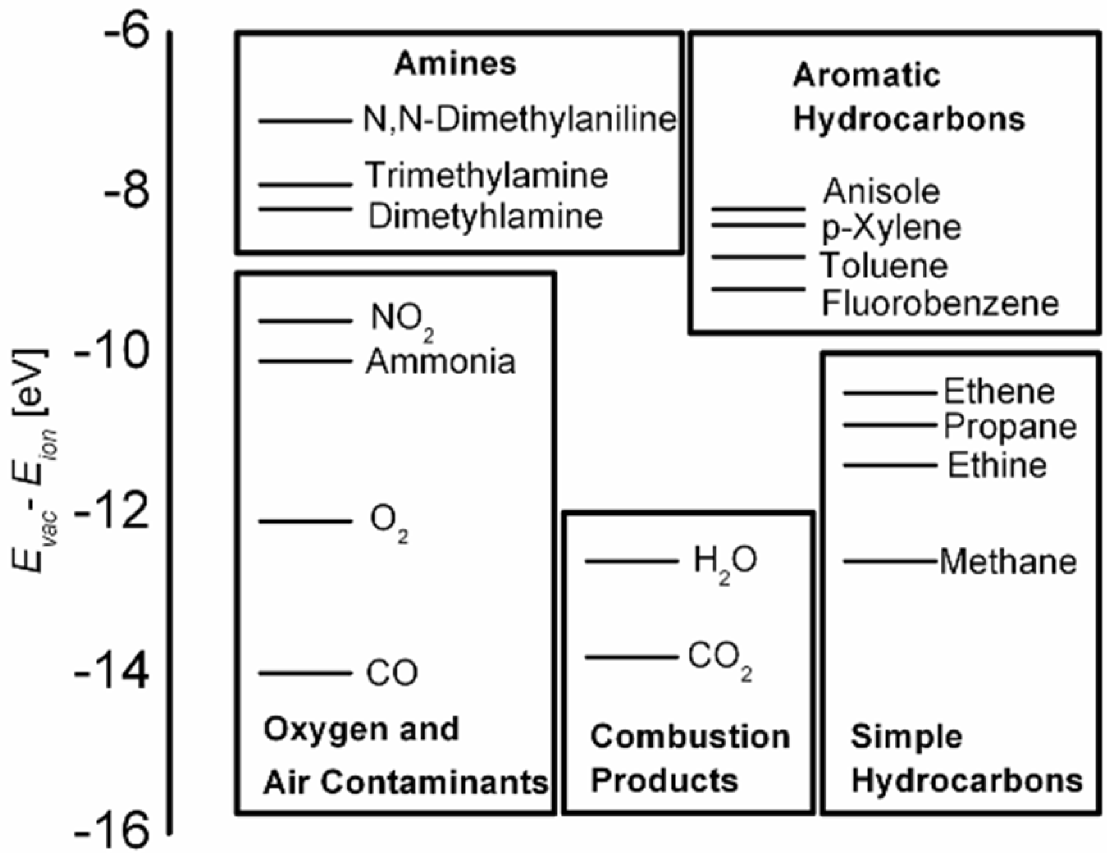


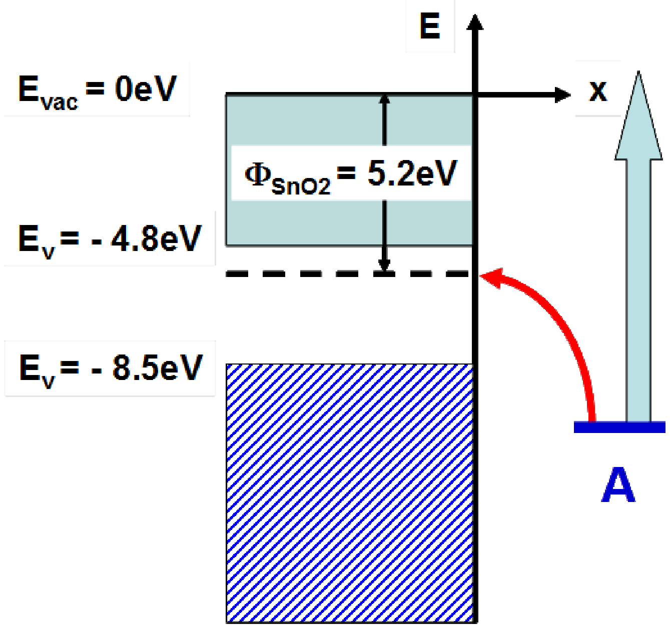


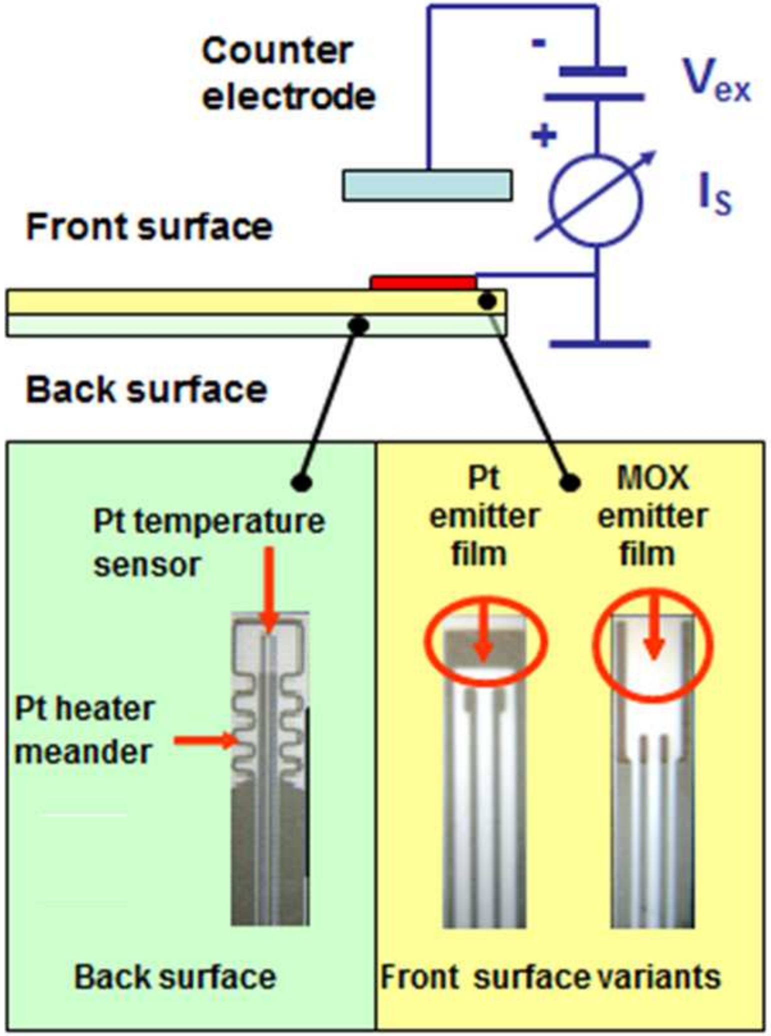
FULLY INTEGRATED
ALL-SOLID-STATE SENSORS
ON MICROMACHINED PLATFORMS:
NEW TYPE OF GAS SENSORS

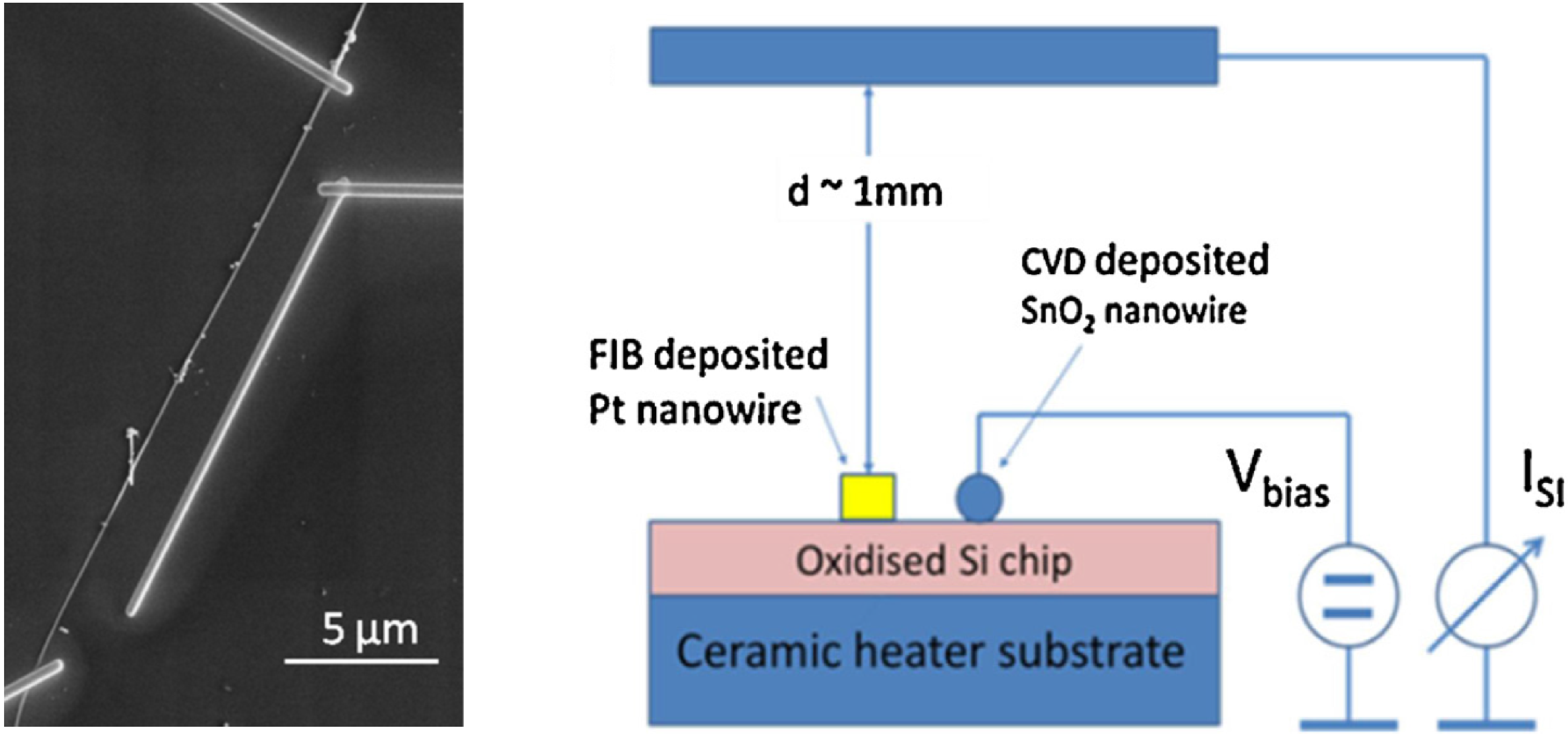
Surface ionization
based on nanostructures

7FP NMP S3

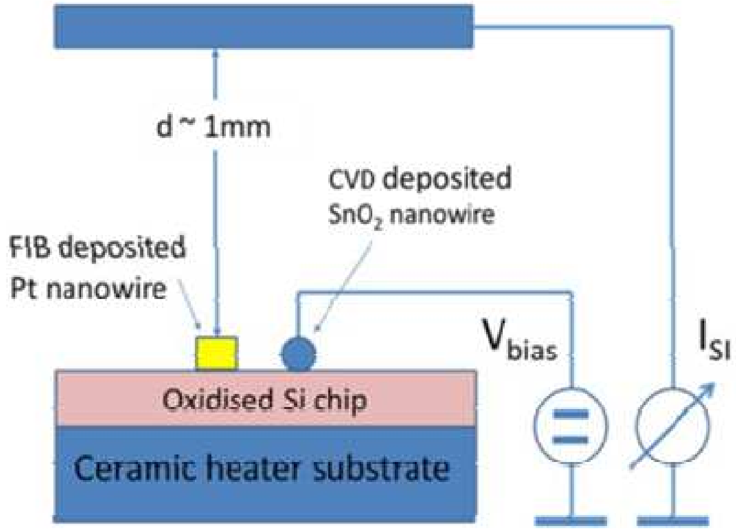

-6
-8
-10
-12
-14
-16
E_{vac} - E_{ion} [eV]
Amines
N,N-Dimethylaniline
Trimethylamine
Dimetyhlamine
Aromatic Hydrocarbons
Anisole
p-Xylene
Toluene
Fluorobenzene
NO2
Ammonia
O2
CO
Oxygen and Air Contaminants
H2O
CO2
Combustion Products
Ethene
Propane
Ethine
Methane
Simple Hydrocarbons

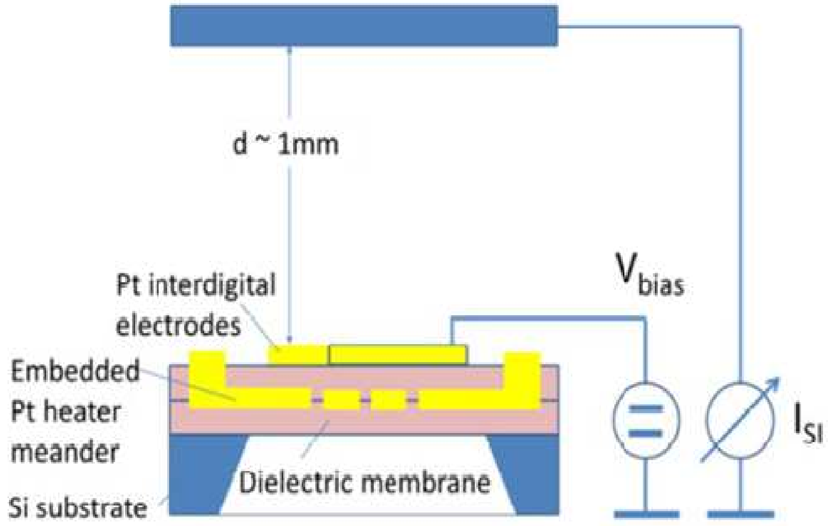

E
x
E_{vac} = 0eV
Φ_{SnO2} = 5.2eV
E_v = - 4.8eV
E_v = - 8.5eV
A

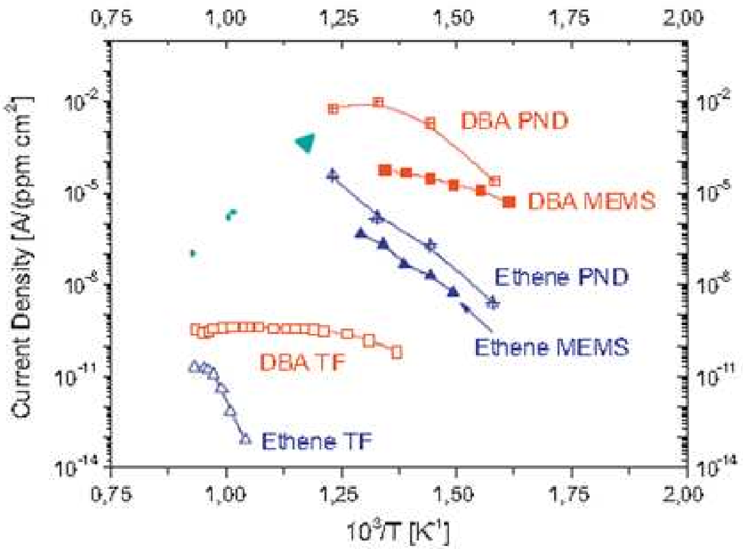

Counter electrode
-
+
Vex
Is
Front surface
Back surface
Pt temperature sensor
Pt heater meander
Back surface
Pt emitter film
MOX emitter film
Front surface variants

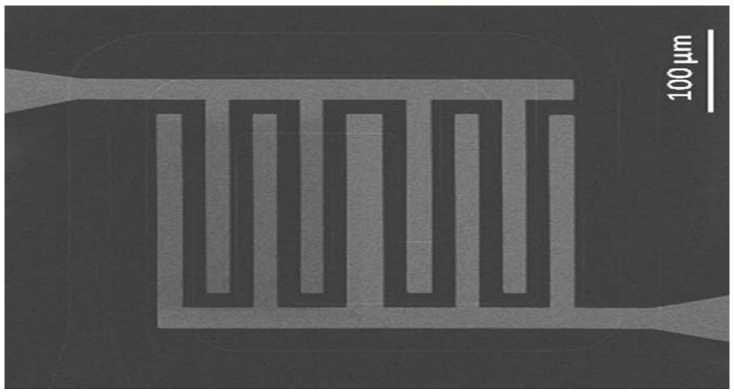


(a) top view onto the parallel nanowire (PNW) chip investigated; (b) vertical readout mode applied to the PNW chip in (a) turning it into a single nanowire (SNW) device. In both modes of readout the PND chip is glued to a ceramic heater substrate carrying a Pt heater meander and a Pt thermometer on its backside









Specific SI emission currents for analytes with different free-space ionization energy EI: DBA (EI = 7.5 eV) and ethene (EI = 10.5 eV) as observed in MEMS, PNDs andTF devices.

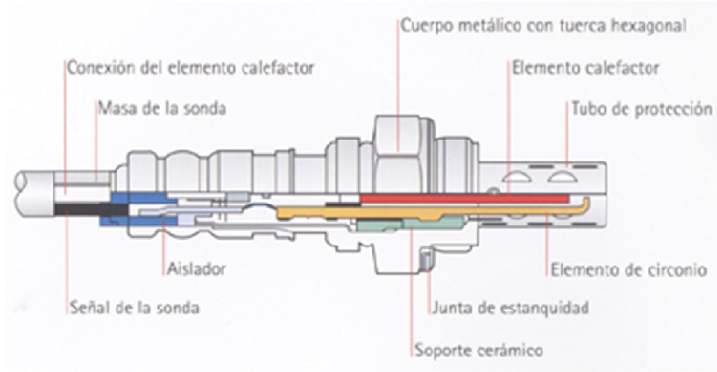
FULLY INTEGRATED
ALL-SOLID-STATE SENSORS
ON MICROMACHINED PLATFORMS:
NEW TYPE OF GAS SENSORS

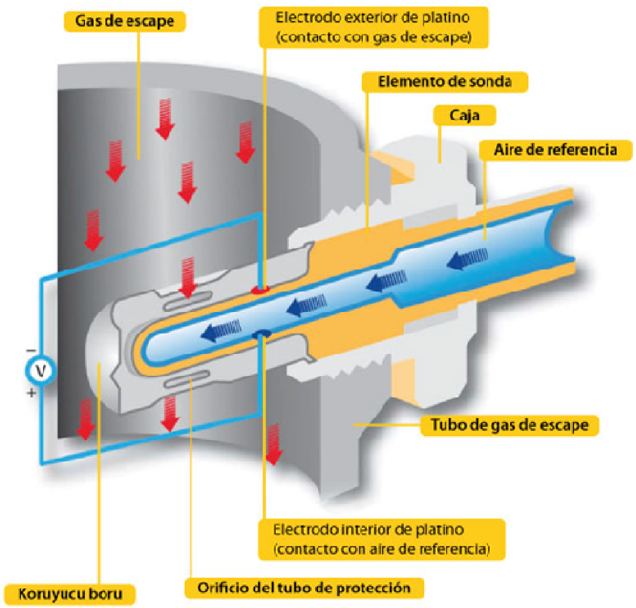
Electrochemical sensors
based on nanoionics

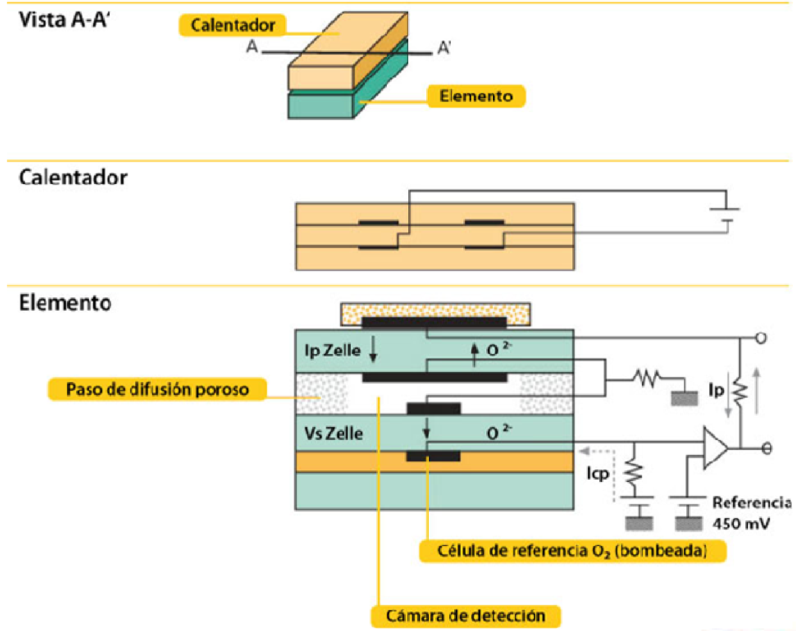
EUROPEAN COOPERATION IN SCIENCE AND TECHNOLOGY

Institut de Recerca en Energia de Catalunya
Catalonia Institute for Energy Research


CO
HC
NOx
SO2
Pb
C

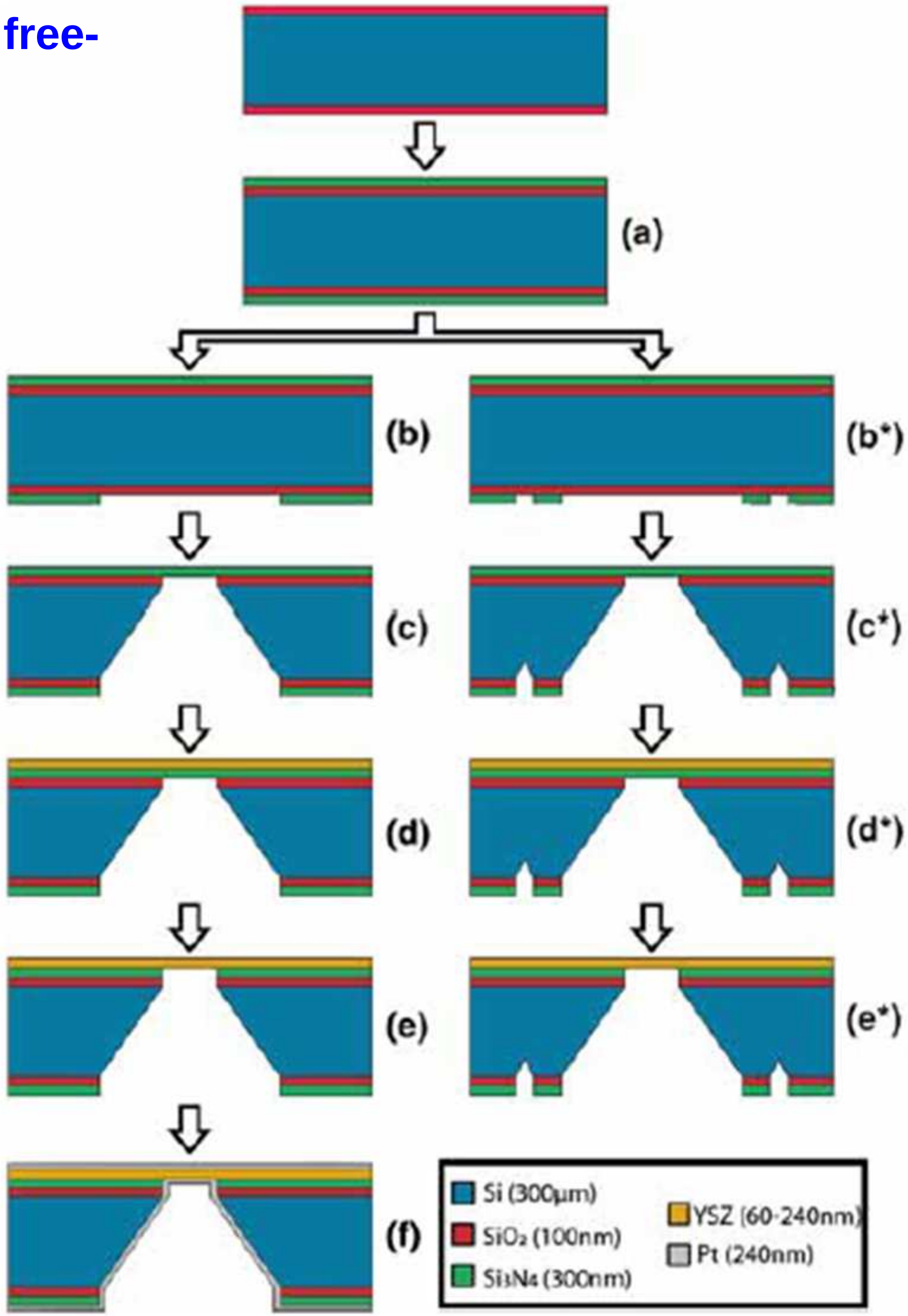

Cuerpo metálico con tuerca hexagonal
Conexión del elemento calefactor
Elemento calefactor
Masa de la sonda
Tubo de protección
Aislador
Elemento de circonio
Señal de la sonda
Junta de estanquidad
Soporte cerámico


Gas de escape
Electrodo exterior de platino
(contacto con gas de escape)
Elemento de sonda
Caja
Aire de referencia
V
Tubo de gas de escape
Electrodo interior de platino
(contacto con aire de referencia)
Koruyucu boru
Orificio del tubo de protección


Vista A-A'
Calentador
A
A'
Elemento
Calentador
Elemento
Ip Zelle
O 2-
Paso de difusión poroso
Ip
Vs Zelle
O 2-
Icp
Referencia
450 mV
Célula de referencia O2 (bombeada)
Cámara de detección

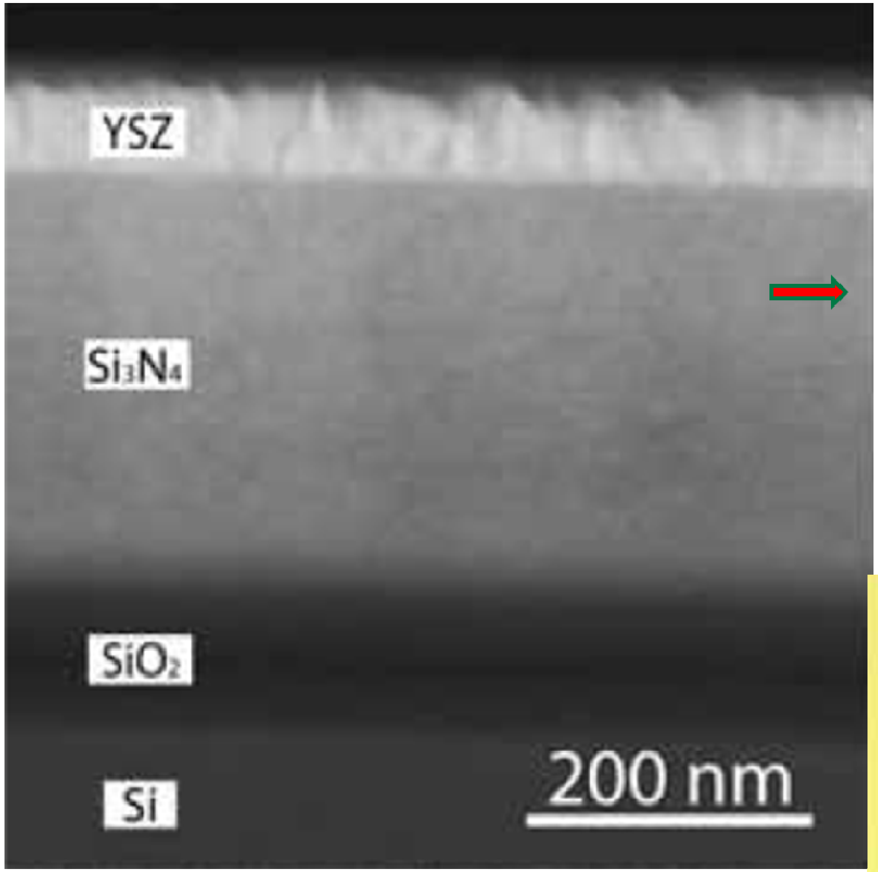
Fabrication process of YSZ free-standing membranes:

deposition of 300 nm Si_3N_4 on both sides of a 300 µm thick silicon wafer 100-nm thermally oxidized;
back side photolithography and silicon nitride dry etching;
silicon oxide and silicon wet etching with HF and KOH, respectively;
deposition of 120 nm YSZ thin layer by PLD;
creation of the self-supported YSZ membrane with a silicon nitride reactive ion etching from the back-side;
deposition of 240 nm Pt layer or electrodes by sputtering.
Parallel steps (marked with stars) refer to the alternative fabrication flow used for membranes compatible with TEM sample holders.



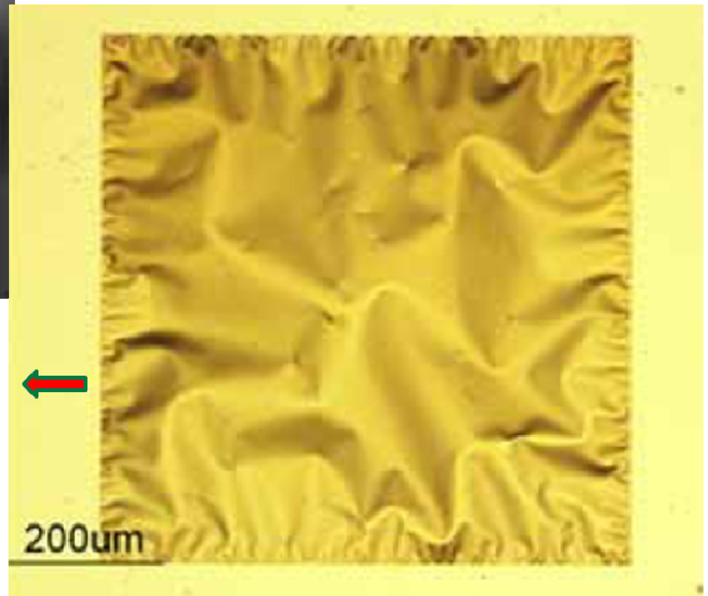
cost
EUROPEAN COOPERATION

IREC
Institut de Recerca en Energia de Catalunya
Catalonia Institute for Energy Research



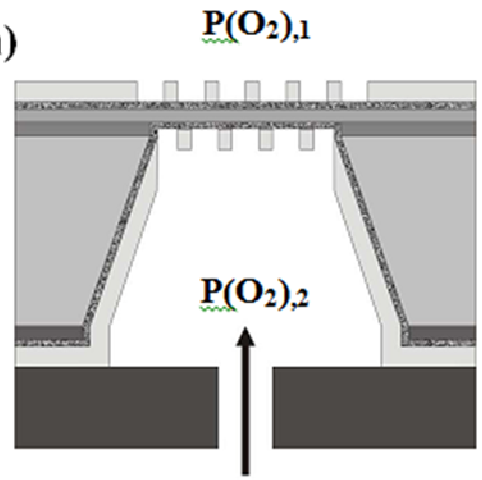
Cross-section SEM image of a 60 nm thick YSZ layer deposited by PLD at 200 °C.

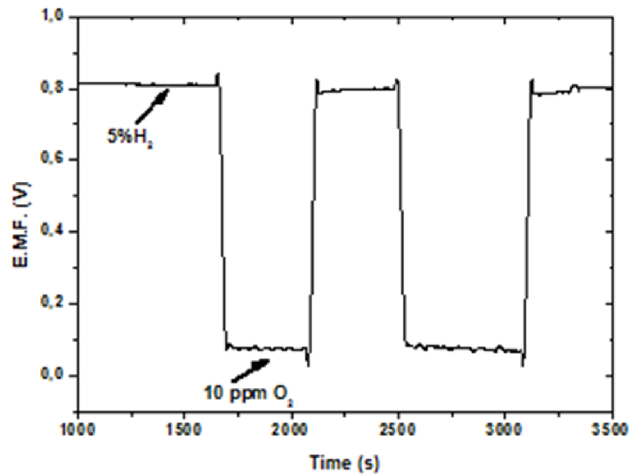
The YSZ layers were deposited on Si/SiO2/Si3N4 substrates.

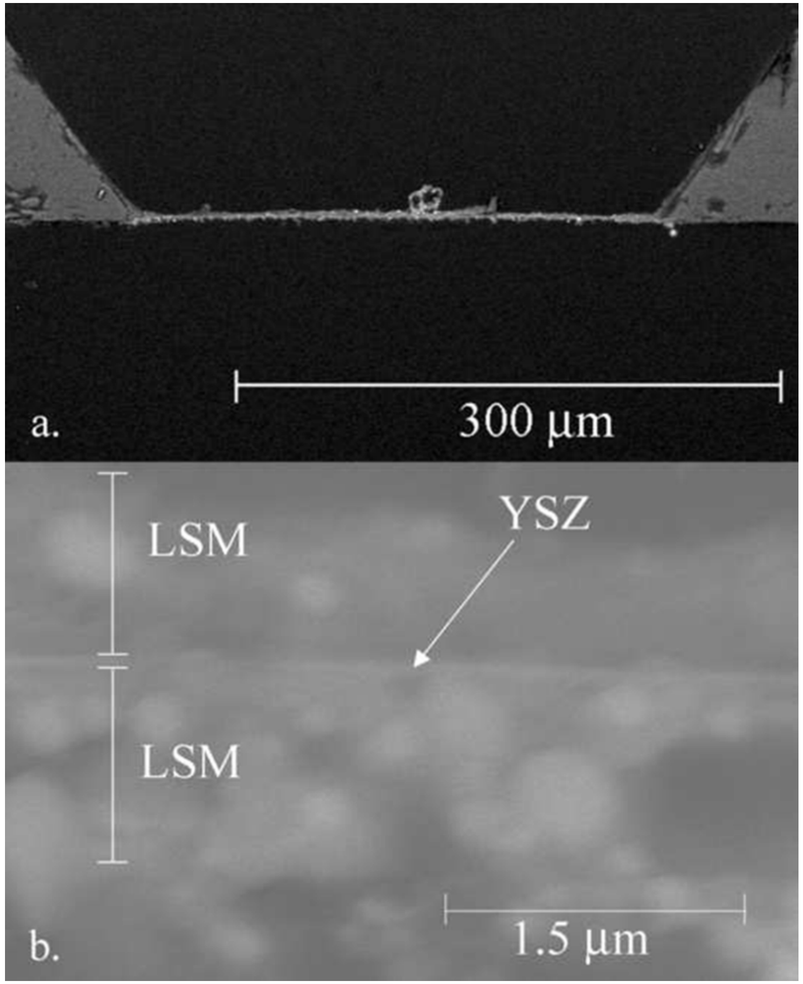


Optical microscope top view image of a typical free-standing YSZ membrane

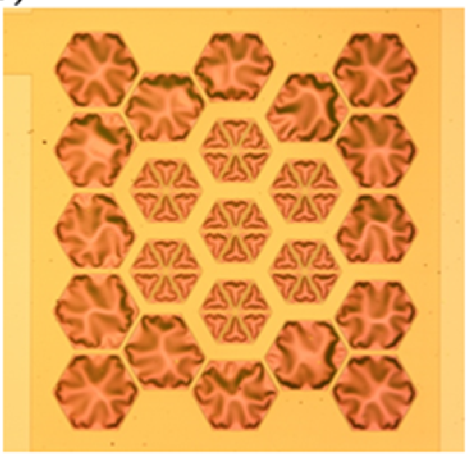
(a)

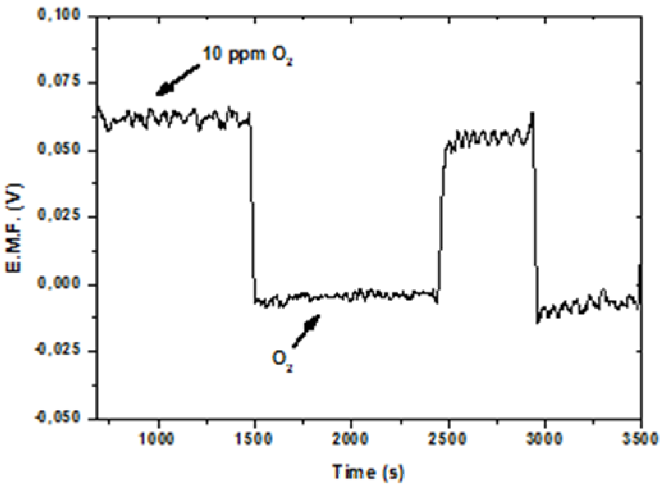

P(O2),1
P(O2),2

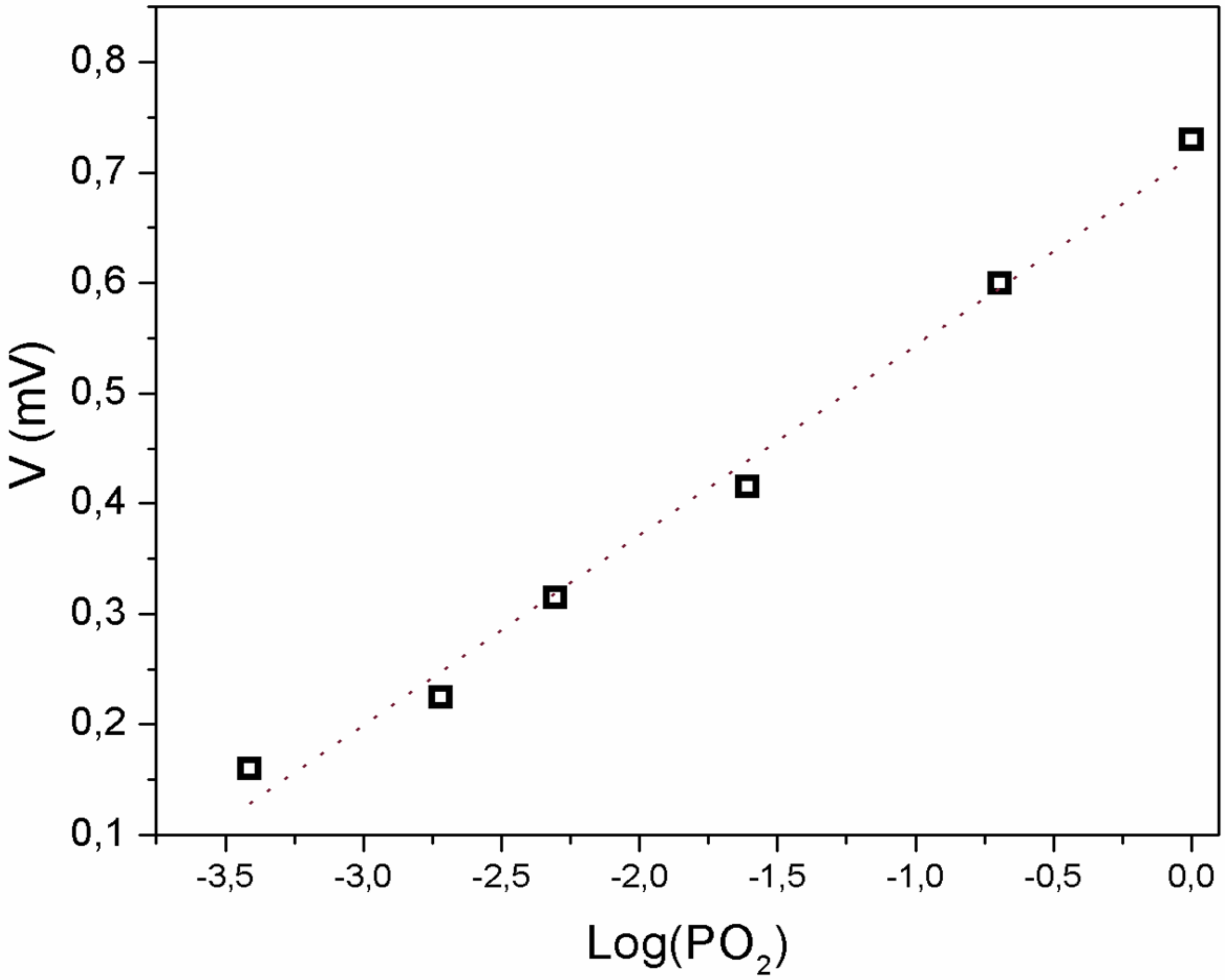

1,0
0,8
0,6
0,4
0,2
0,0
E.M.F. (V)
5%H2
10 ppm O2
1000
1500
2000
2500
3000
3500
Time (s)


a.
300 µm
b.
LSM
YSZ
LSM
1.5 µm

(b)




0,100
0,075
0,050
0,025
0,000
-0,025
-0,050
E.M.F. (V)
10 ppm O2
O2
1000
1500
2000
2500
3000
3500
Time (s)


0,8
0,7
0,6
0,5
0,4
0,3
0,2
0,1
V (mV)
-3,5
-3,0
-2,5
-2,0
-1,5
-1,0
-0,5
0,0
Log(PO2)

Micro and Nanotechnology are changing the perspective in the field of integrated gas sensors:

Conductometric gas sensors based on nanostructures growth or deposited on hotplates open new pathways.

Surface ionization is also improving performances due to the temperature and field effects at the nano scale level defined by nanostructures managed by high temperature hot plates.

Fully integrated electrochemical gas sensors based on nanoionics characteristics of the a thin solid electrolyte layer and its control based on high temperature hot plate are also changing the future in this field.

RESULTS and future activities

•Micro and Nanotechnology are changing the perspective in the field of integrated gas sensors

•Conductometric gas sensors based on nanostructures growth or deposited on hotplates open new pathways.

•Surface ionization is also improving performances due to the temperature and field effects at the nano scale level defined by nanostructures managed by high temperature hot plates.

•Fully integrated electrochemical gas sensors based on nanoionics characteristics of the a thin solid electrolyte layer and its control based on high temperature hot plate are also changing the future in this field.

Future planned Activities

- Pulsed mode operation instead isothermal working mode improves the characteristics of conductometric gas sensors, as non expensive devices. Selectivity and sensor response are improved allowing better measurement of CO, NH3, NOx, …….
- Surface ionization based sensors improve also selectivity
- Fully integrated electrochemical are very promising Pat. Nº P26999ES01

All these new options need to be explored to evaluate the full feasibility of these new approaches

CONCLUSIONS

- Micro and Nano technology open news alternatives based on the use of high temperature hotplates.
- Low cost fully integrated alll solid state integrated gas sensors based on metal oxides but using different sensing mechanisms

  conductometric

  surface ionization

  electrochemical

  are potential candidate as air quality monitoring elements.
- Likewise, these news technological approaches open news sensing operation modes, due to the very short response time of these systems. Moreover their combination allows the application of new algorithms improving the discrimination between interfering gases for a better air quality assessment and monitoring.