Chemical NanoSensors and Microsystems for Air Pollution Detection

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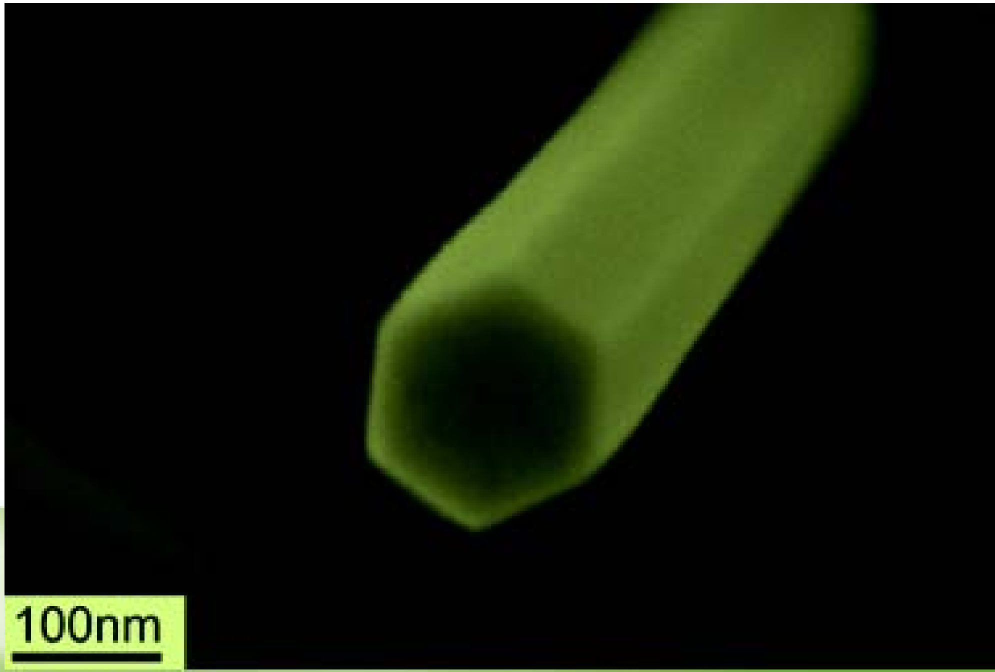
IMCS2012-Cost session

Outline

- Introduction and motivation
- From sensors to microsystems
- Sensing versus Monitoring Air quality
- New potential devices based on Advanced Sensing Materials
- Conclusions



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From Macro to micro and from micro to nano:
New phenomena and mechanisms

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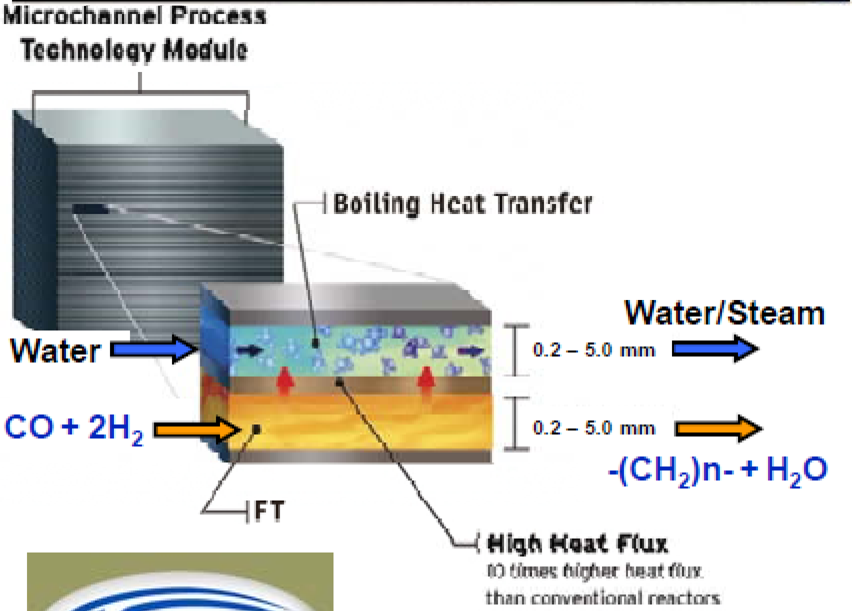
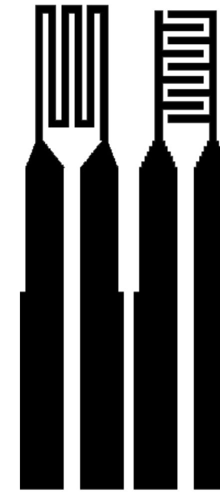
http://www.velocys.com/docs/Microchannel_FT_White_Paper_Sep08.pdf

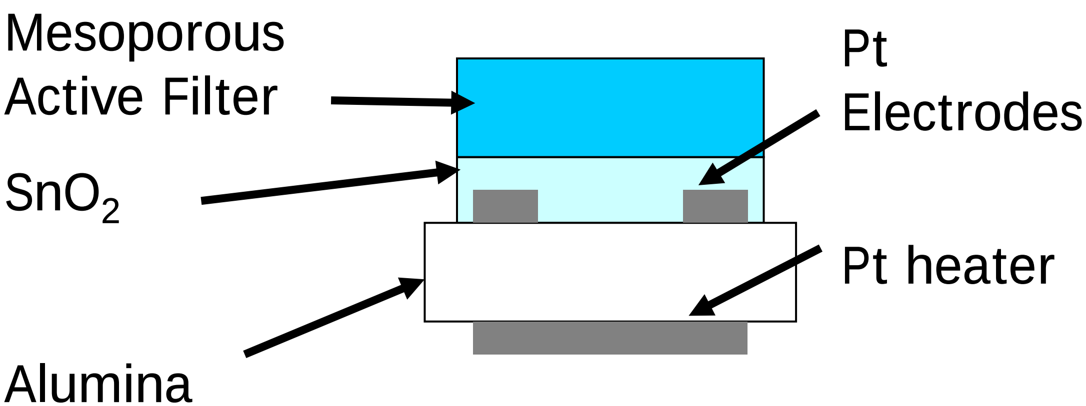
MEMS: Great success of the multi functional integrated systems in size reduction

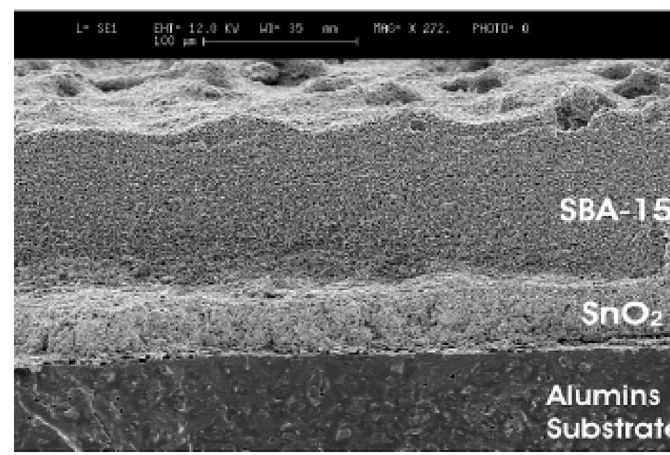
Conventional Fischer-Tropsch Synthesis reactor SASOL





Active sensing material **SnO_2** impregnated with **Pd** and **Pt** for screen printed sensors.





5 Volts and more than 200 mA

Thin Solid Films 436 (2003) 64-69

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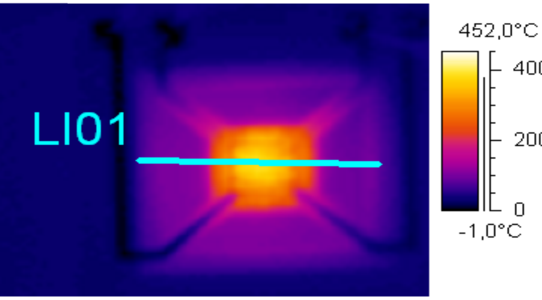
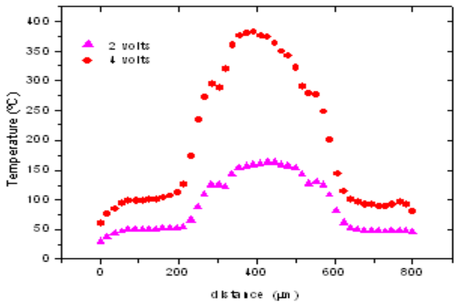
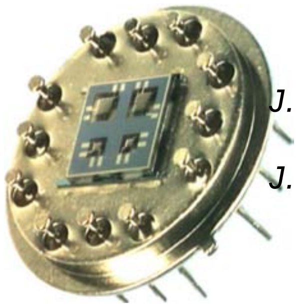
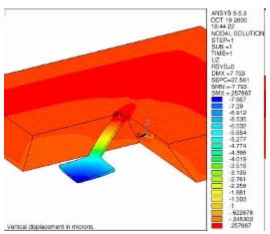
Sensing platforms

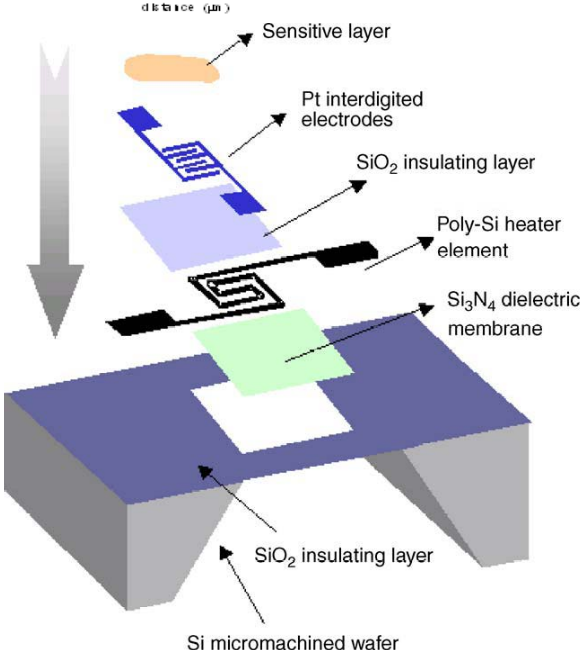


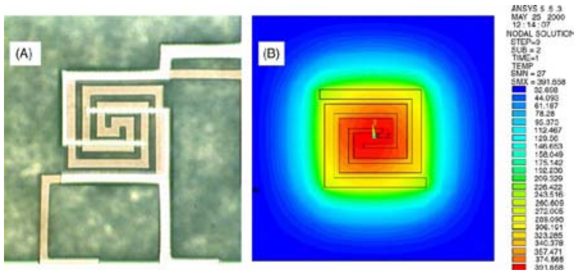


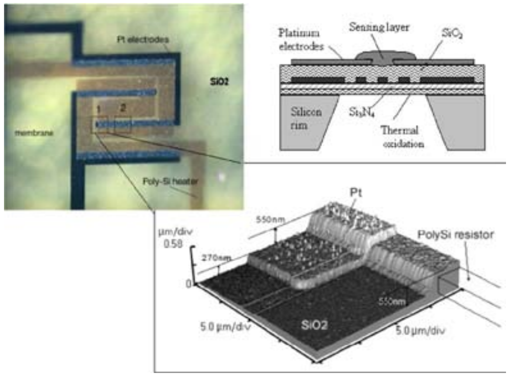


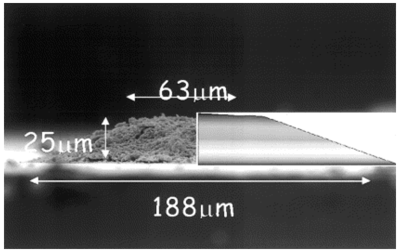
SNB **84**, 60 (2002)
SNB **95**, 275 (2003)
J. Micromech. Microeng. **13**, S119 (2003)
J. Micromech. Microeng. **13**, 548 (2003)
SNB **114**, 826 (2006)
SNB **114**, 881 (2006)











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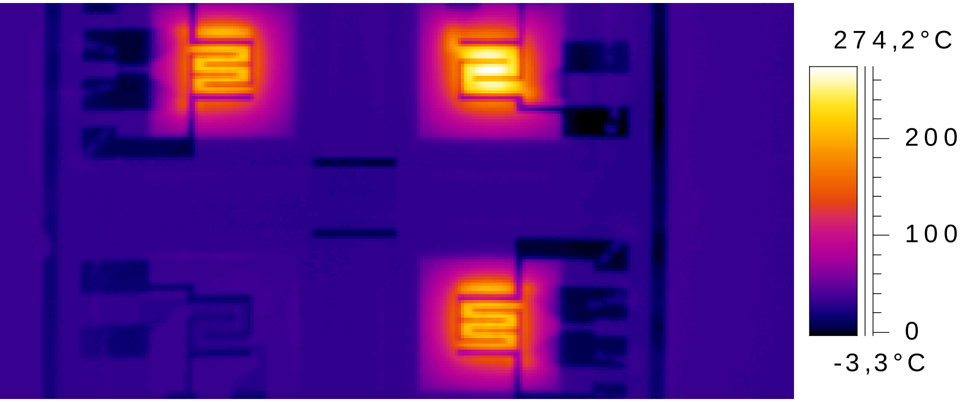
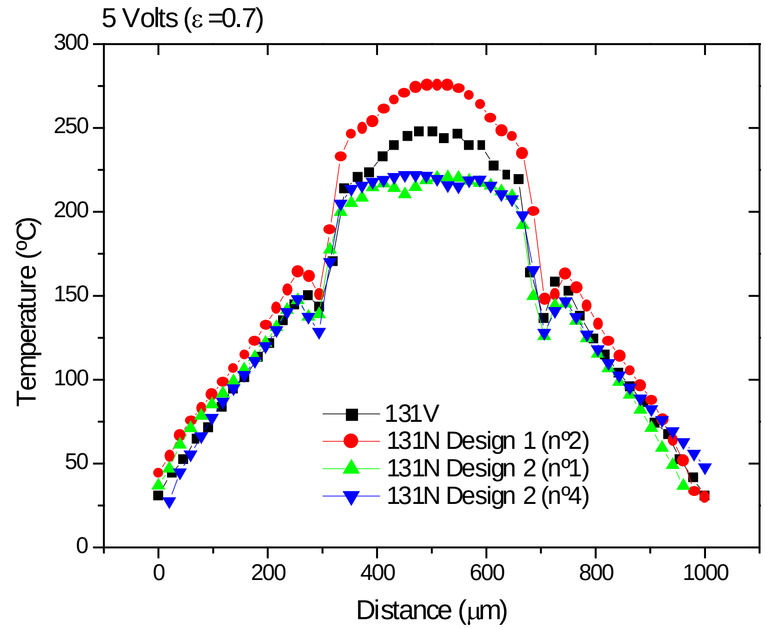
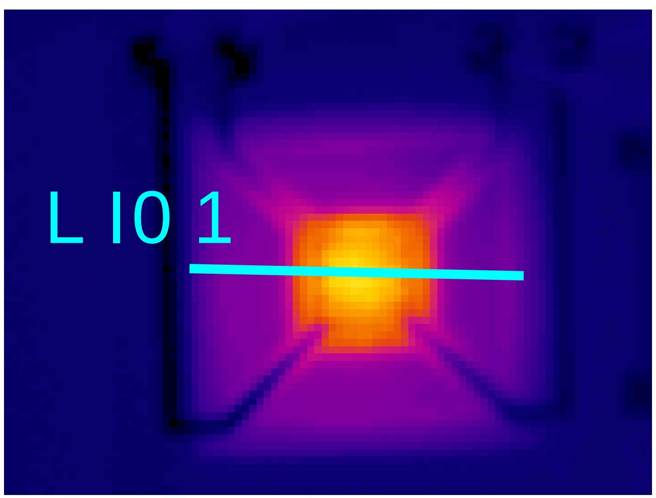
micromechanized gas sensor platforms



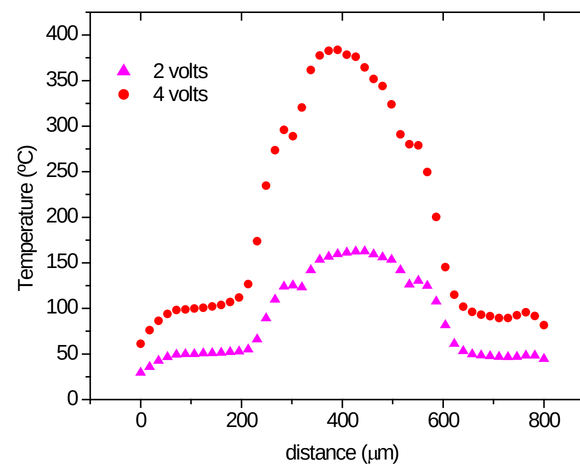


6ºC/mW
Rise time < 15 ms

Power < 70 mW



8ºC/mW power requirements < 50 mW
Rise time < 10 ms



J of Micro M&E (2004)

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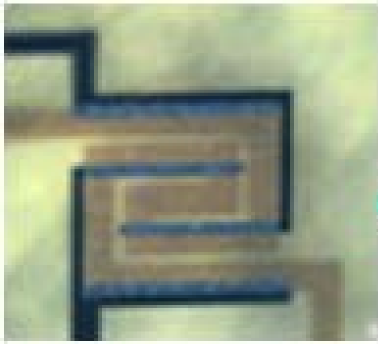

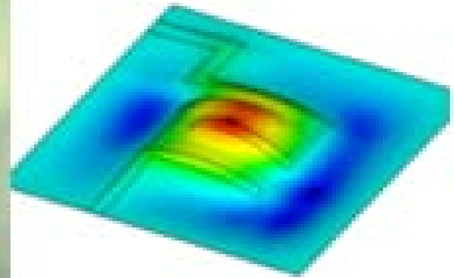

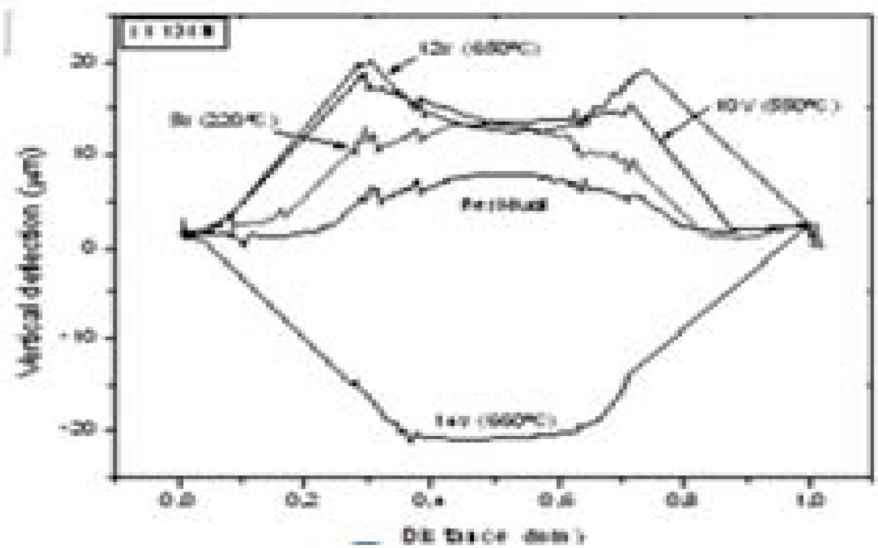

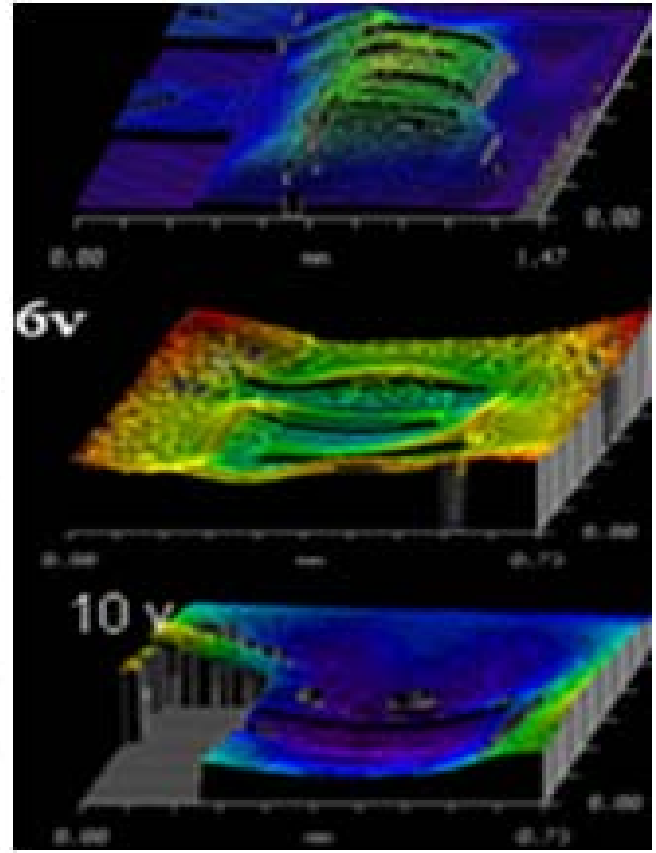

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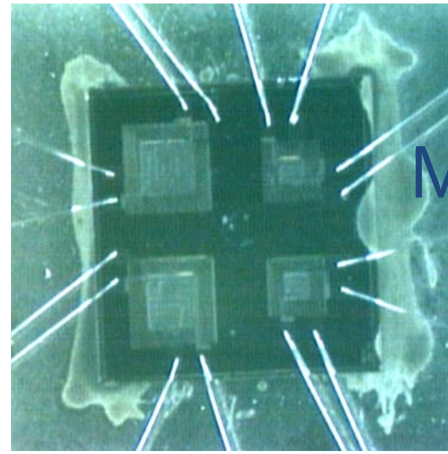
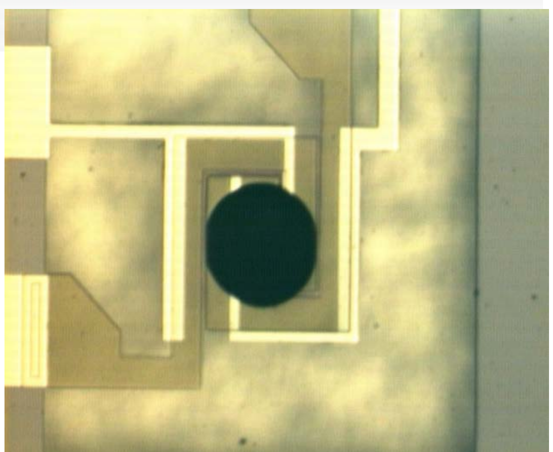
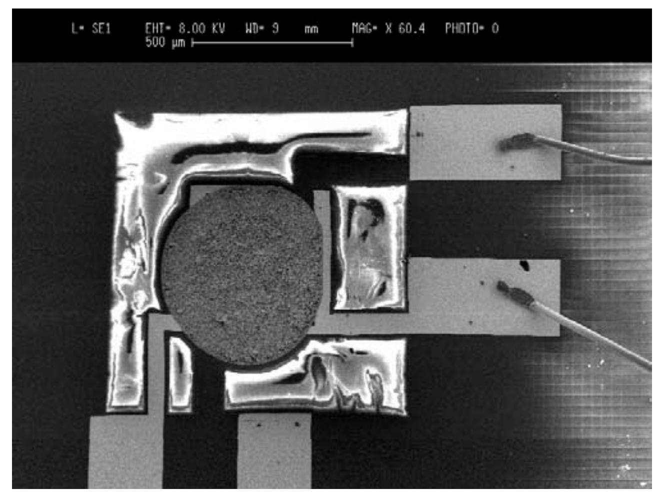
What about the "functional" materials?



Multi -Sensors





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Requirements for environments and quality of air control are every time harder

However, there is a gap between gas alarms and gas monitors systems.

Gas alarms are required to detect securely a target gas before its concentration reaches a fatal level.

Gas monitors, on the other hand, is required to monitor a selected gas as precisely as possible.

This requirement has been rather hard to be met by a semiconductor sensor because its resistance in air (base resistance) tends to suffer from drifting more or less depending on the humidity surrounding it or having surrounded it.

In this scenario, humidity has been known as one of the most typical disturbing gases to the sensors.

It is well know that on increasing humidity in ambient air the base resistance is reduced significantly, accompanied by a loss in the response to a target gas.

This is a moisture effect appearing instantly masking or hidden the truly sensor response (immediate effect). Typical example the huge difficulty to distinguish between less than 50 ppm of CO and humidity effects.

However, for continuous monitoring, a further complication exist in many ambients usual in many cities and countries.
It has been recognized by experts that high humidity in summer tends to cause the base resistance to shift up to a level so called summer resistance, while low humidity in winter tends to cause an opposite effect, winter resistance.

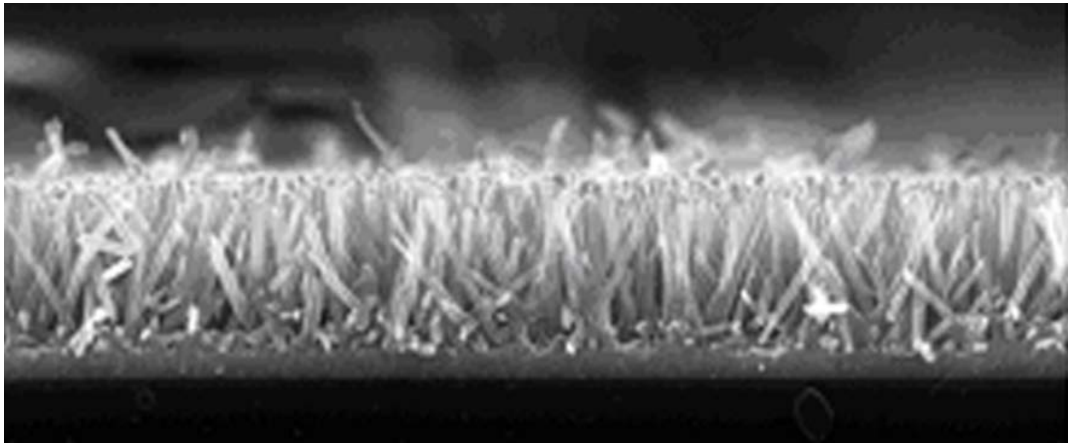
This is a humidity effect appearing in a long term as the cycle of the seasons and altering the resistance baseline in an accumulative way or wear-out effect.

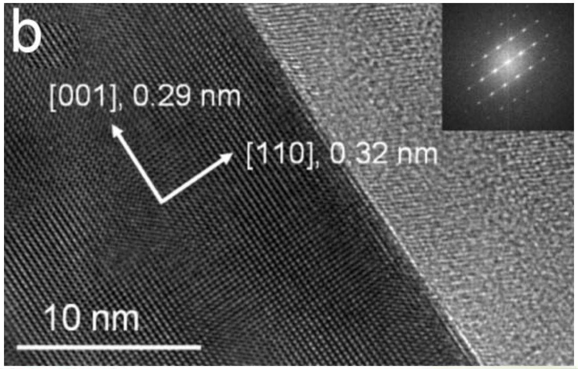
So, in order to improve the precision of gas monitoring and to success on it, there is several challenges:

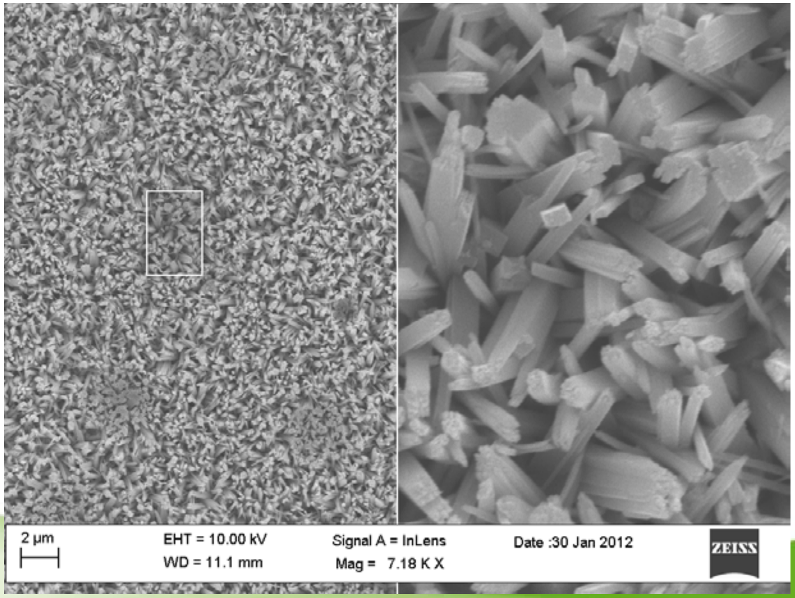
- To eliminate these humidity crossing effects in an effectively way
- To find a way to calibrate them.

Various attempts have been made empirically to mitigate the humidity effects almost without success, because there has been a lack of a theoretical base on which way the water molecules affect the resistance of the sensing material.

- To knowledge and understand the chemical to electrical transduction mechanisms associated to the water molecules becomes outstanding
- As well as to analyze their interfering and competitive mechanisms with other target molecules required to be detected for air quality monitoring like CO, NO2, etc…







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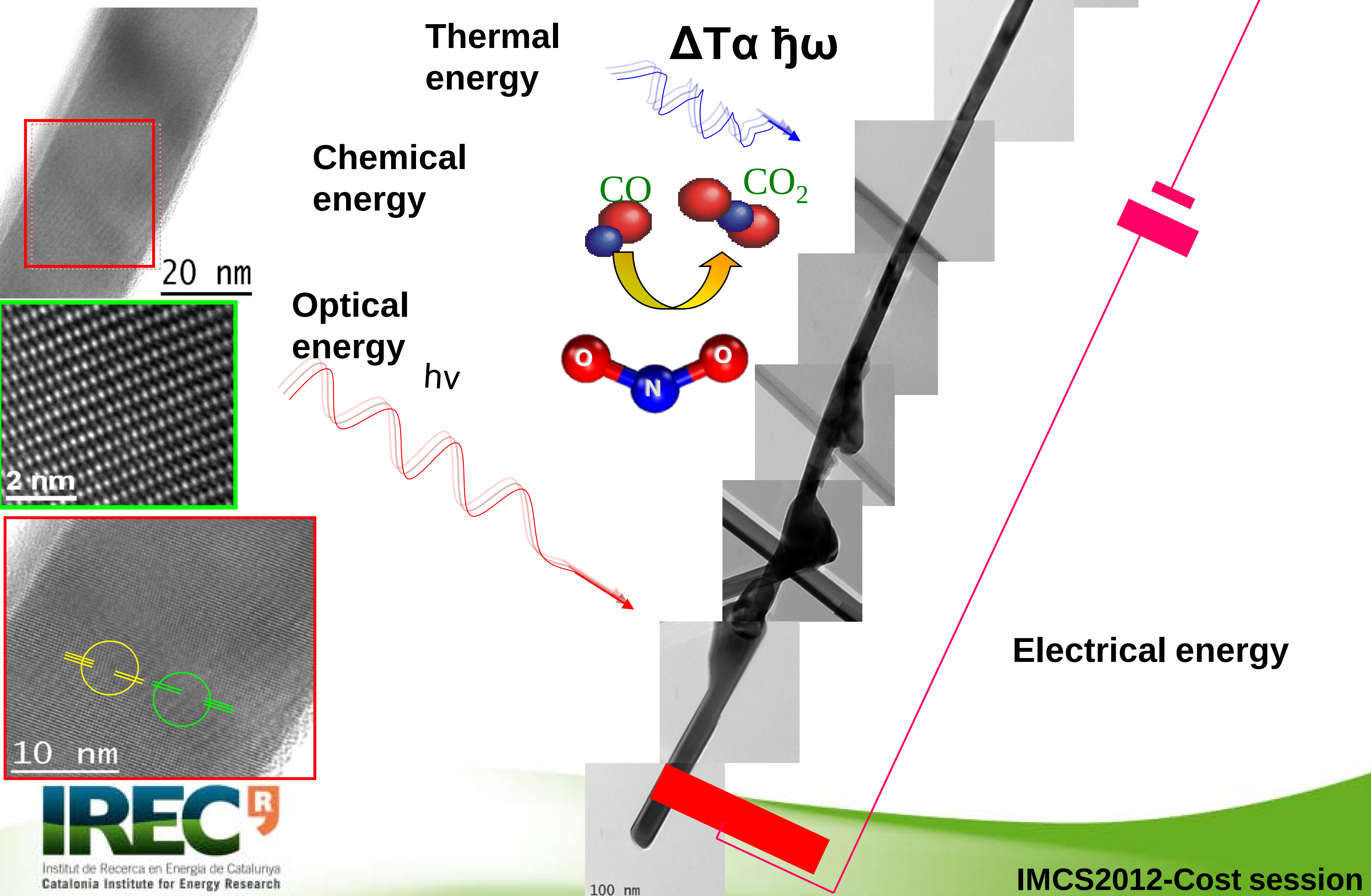
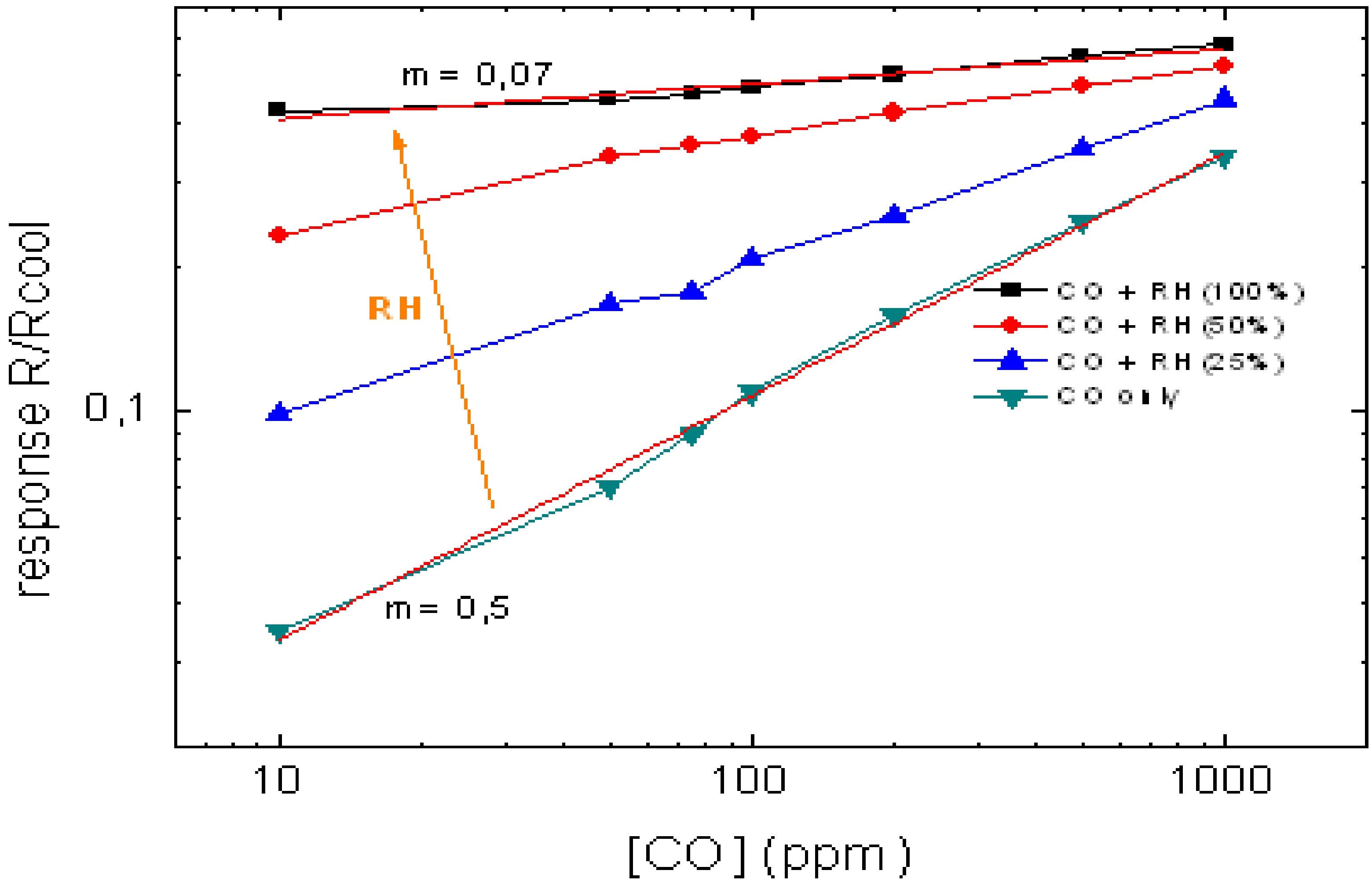
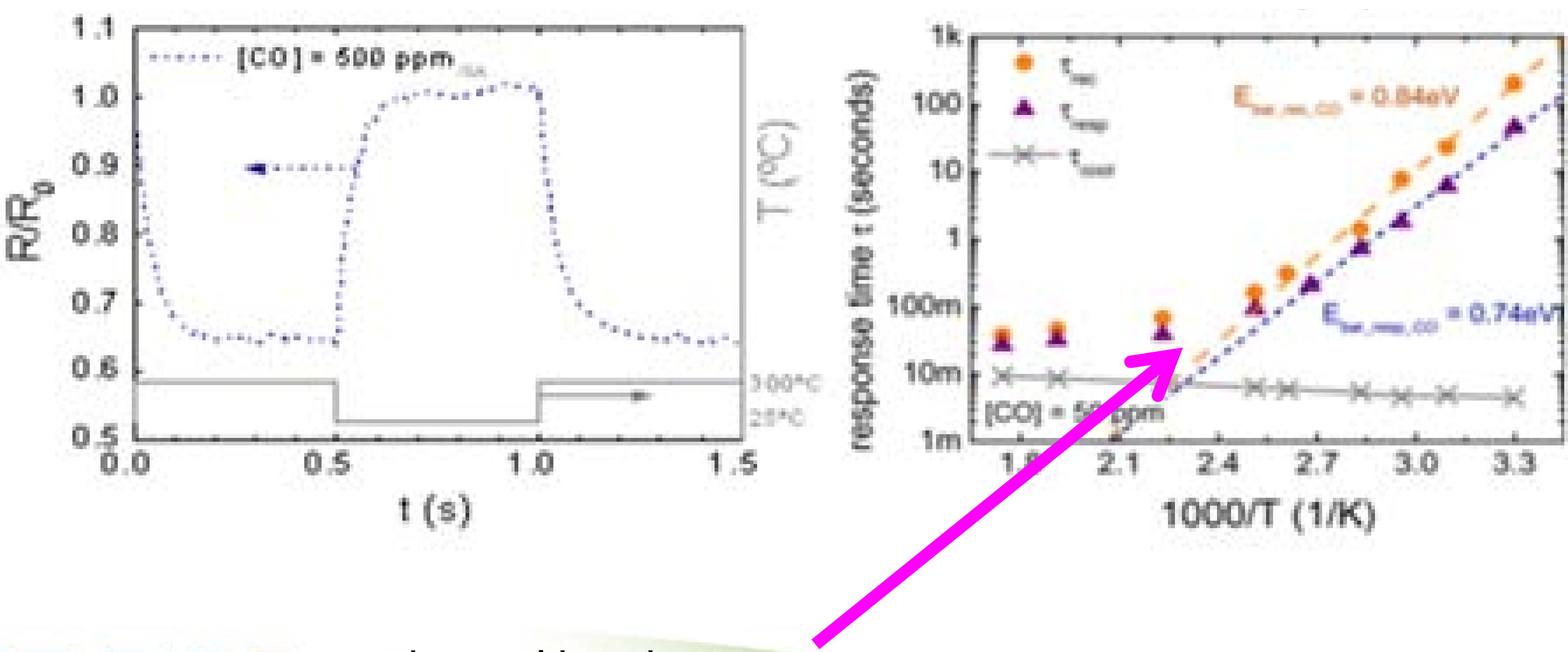
Transduction mechanisms and energy conversion can be better studied using monocrystal at the nanoscale




m = 0,07
RH
m = 0,5
CO + RH (100%)
CO + RH (50%)
CO + RH (25%)
CO only
0,1
response R/Rcool
10
100
1000
[CO] (ppm)

Rise and decay times determination bellow thermal inertia time:

a) Hot gas sensor platforms
b) Individual nanowires by self-heating.



Thermal inertia

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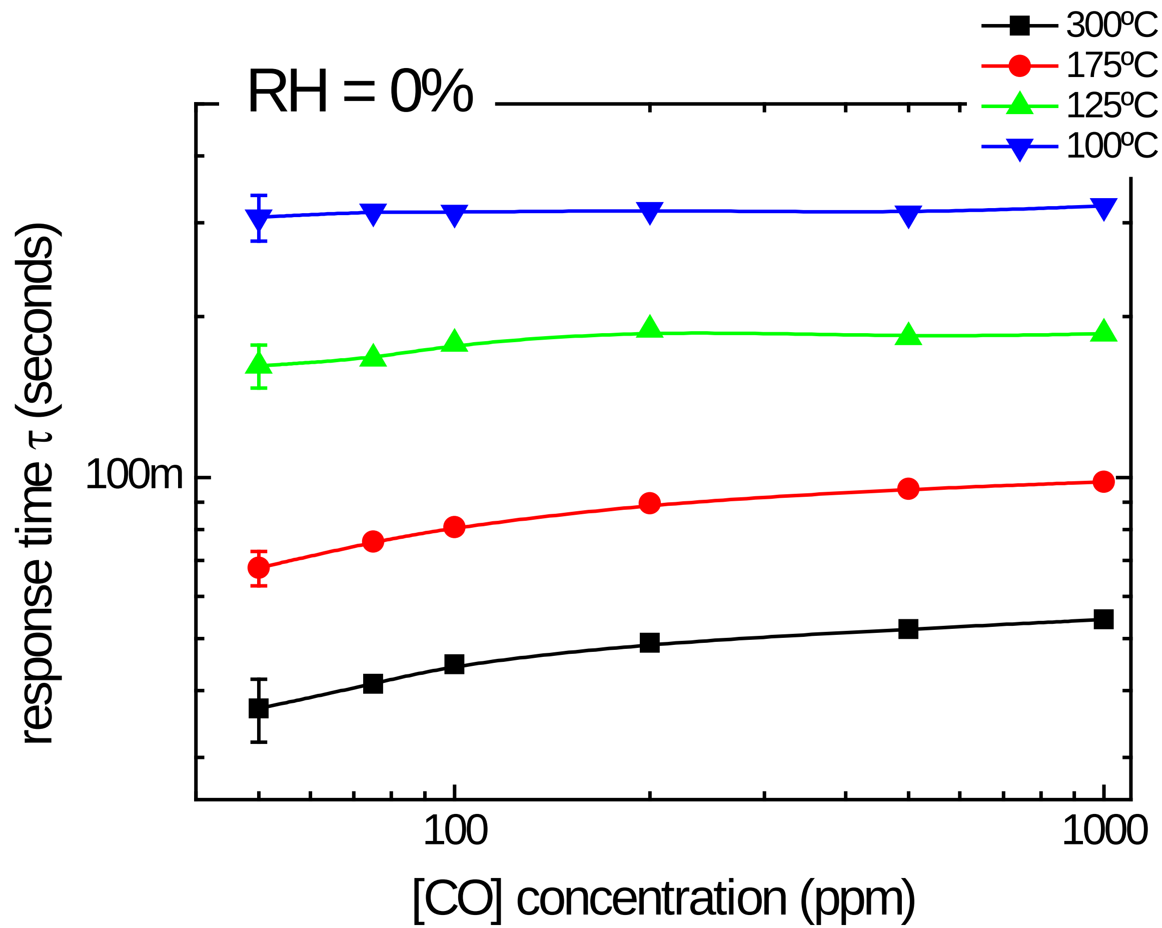
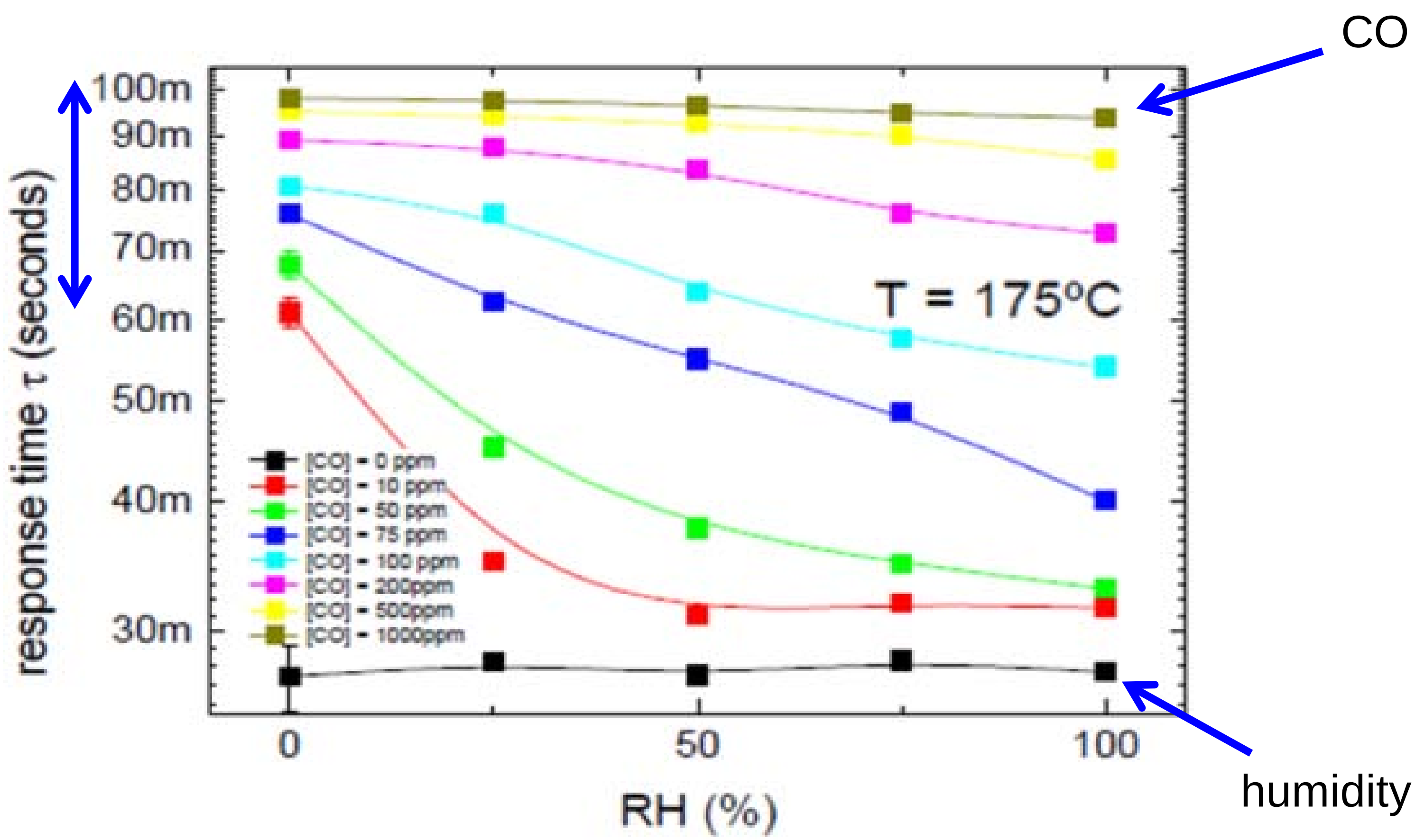
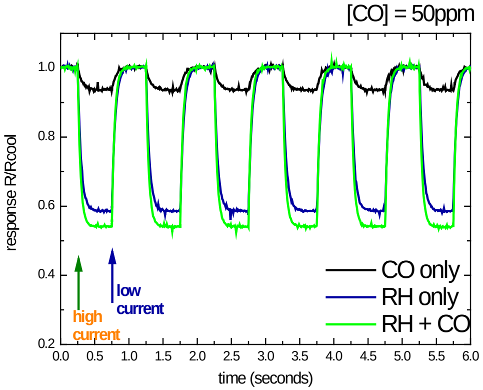
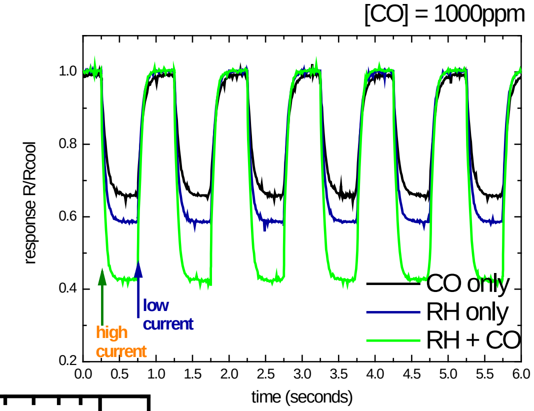
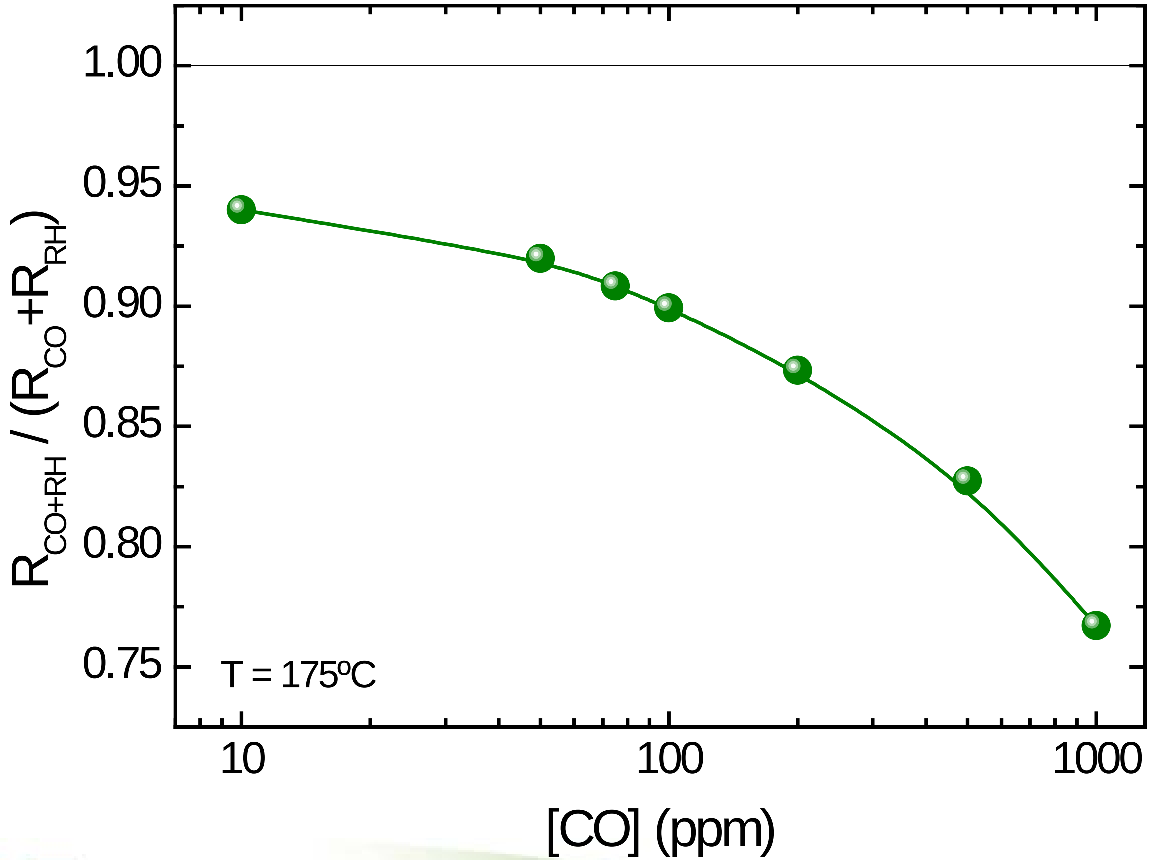


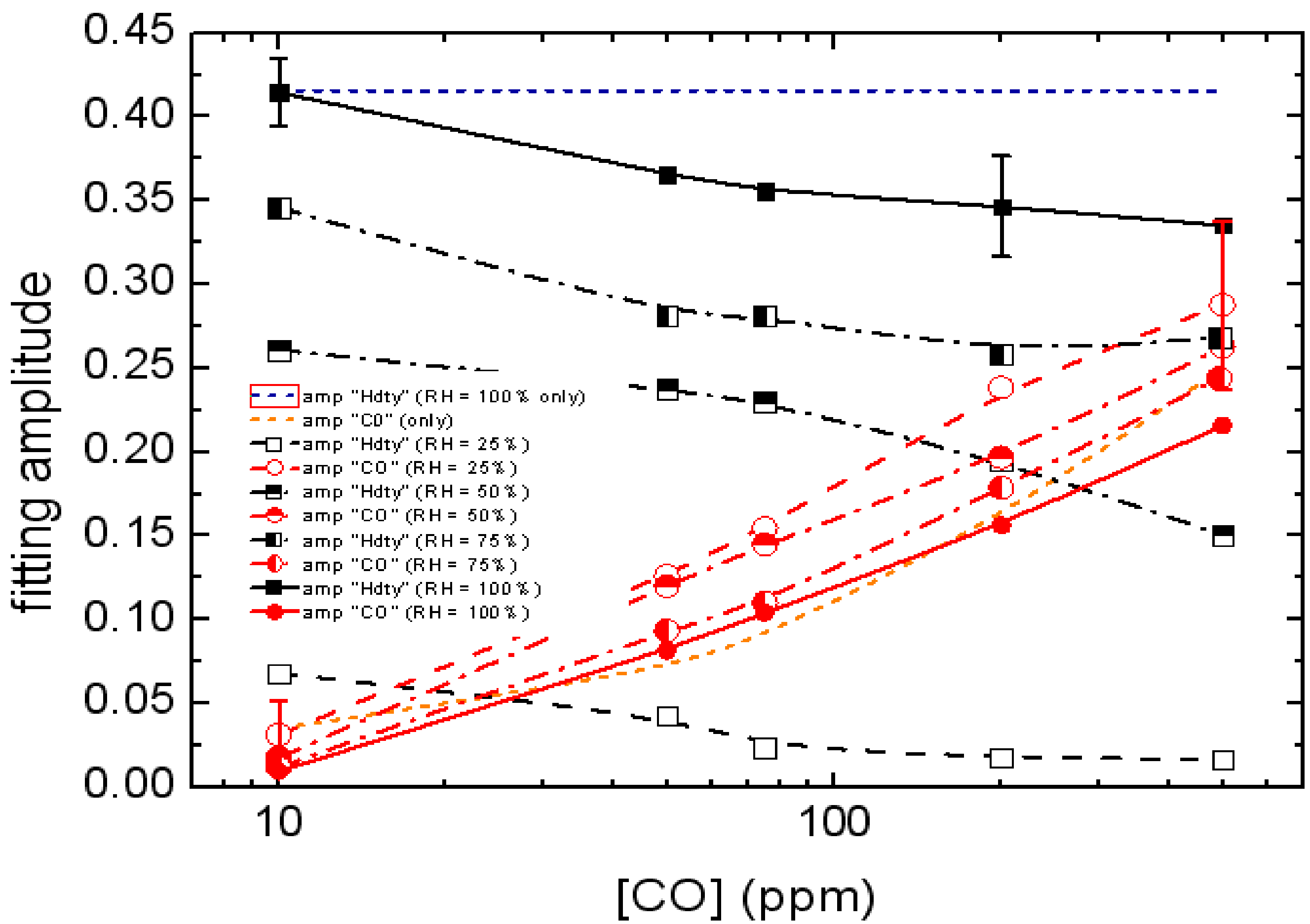
Different sites: two contribution increasing as temperature increases


CO
100m
90m
80m
70m
60m
50m
40m
30m
response time τ (seconds)
T = 175ºC
[CO] = 0 ppm
[CO] = 10 ppm
[CO] = 50 ppm
[CO] = 75 ppm
[CO] = 100 ppm
[CO] = 200ppm
[CO] = 500ppm
[CO] = 1000ppm
0
50
100
RH (%)
humidity


[CO] = 50ppm
response R/Rcool
time (seconds)
CO only
RH only
RH + CO
high current
low current


[CO] = 1000ppm
response R/Rcool
time (seconds)
CO only
RH only
RH + CO
high current
low current


R_{CO+RH} / (R_{CO}+R_{RH})
[CO] (ppm)
T = 175ºC



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Conclusions:

•Air quality detection systems require to monitorize the ambient.

•For it, interfering gases must be avoided and mainly and essentially as first big problem is to avoid humidity influence.

•CO is reacting with the SnO_2 surface observing two different site types in the range of 150-230ºC

•Water molecule is competing with other gases molecules like CO for the same sites. So, for the same humidity concentration the effects are found to depend on the CO gas concentration.

• Critical discrimination happens as CO concentration is low, less than 100 ppm

• Pulsed working modes using advanced very low thermal inertia platform can help to discriminate

• Alternatively, catalytic additive can also help in the competition between CO and Water molecules.

•Humidity discrimination challenge need to be overcome.

Mercès per la vostra atenció!
Gracias por vuestra atención!
Thanks for your attention!

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Patronos:

Prof. J.R.Morante
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Motivation

Energy transfer mechanisms take place at the nano scale level

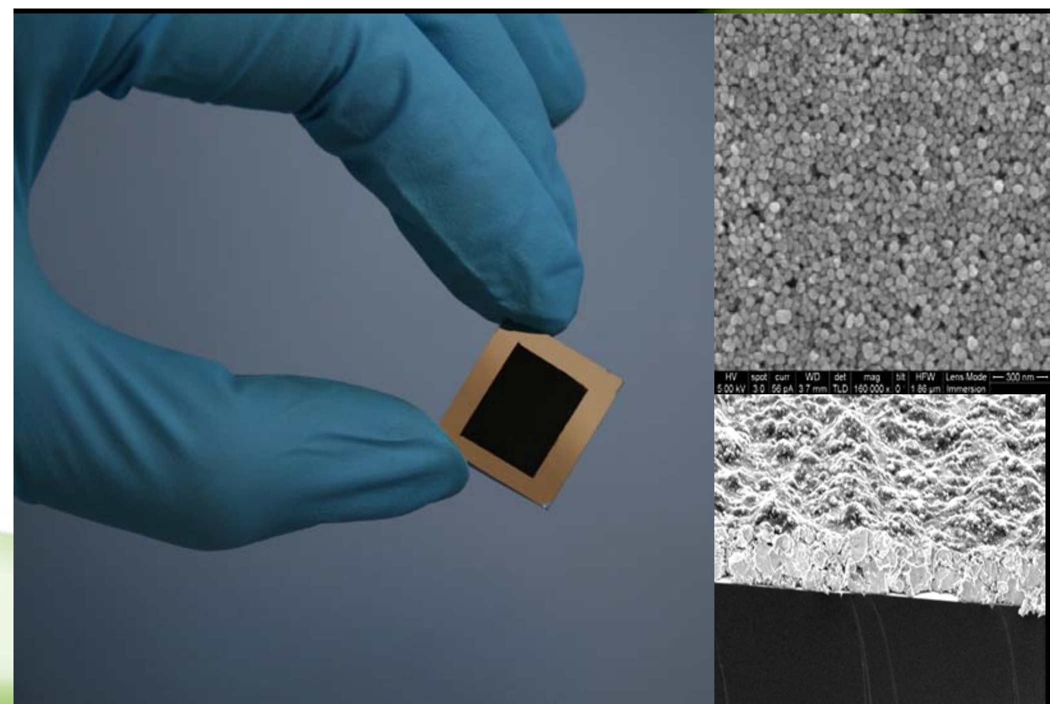
Optical energy (Photons) ⟶ Electrical energy (PV,TI,…)

Optical energy (Photons) ⟶ Chemical energy (PC,PCE,…)

Thermal energy (Phonons) ⟶ Electrical energy (Thel.,…)

Chemical energy ⟶ Electrical energy (Chem. sensors,...)

Electrical energy ⟶ Thermal energy (Selfheating,….)



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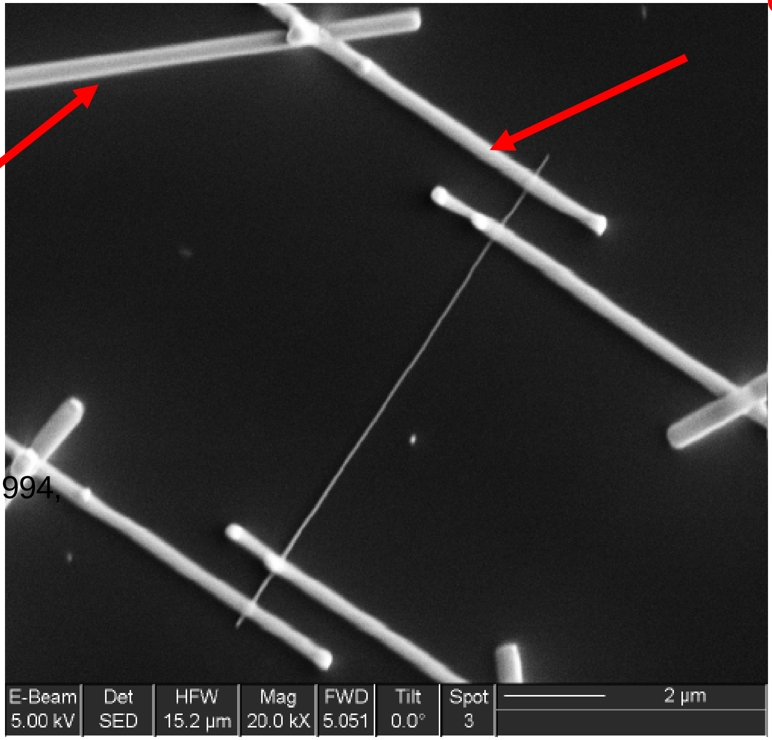
Nanometrology using a single nanowire

Nanofabrication: botom-up approach

- ✓ **Immediate test of novel materials**

Nanotechnology **17**, 5577 (2006)

- ✓ Nanowires contacted with e^- & i^- beam **FIB nanolithogaphy**



Nanotechnology, 18(49) 2007
Advanced Functional Materials 18,2990-2994,

(2008)

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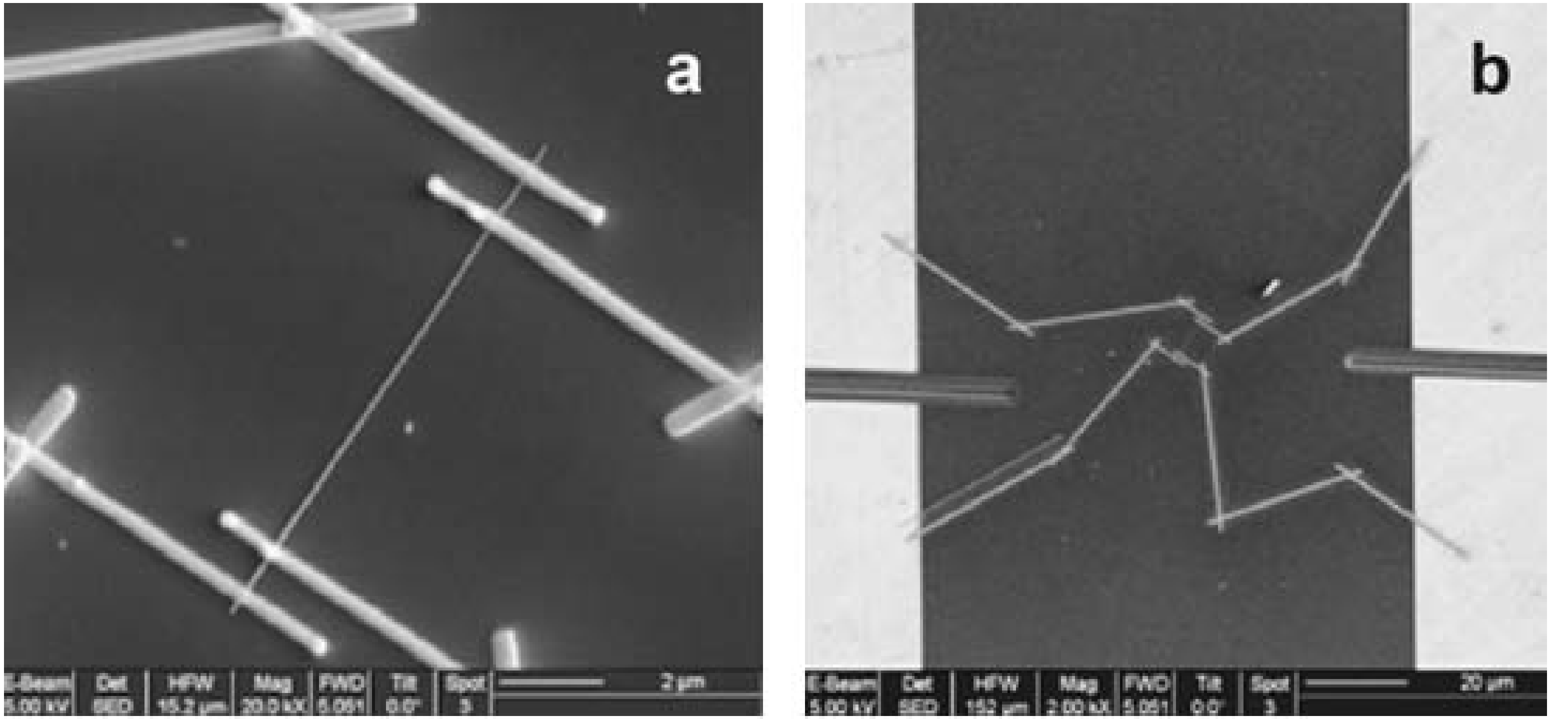

Figure 1 (a) Detail of a singleSnO2 nanowire with four contacts and (b) connection Stripes between the nano and microelectrodes.

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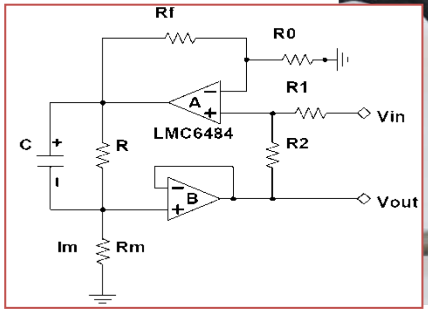
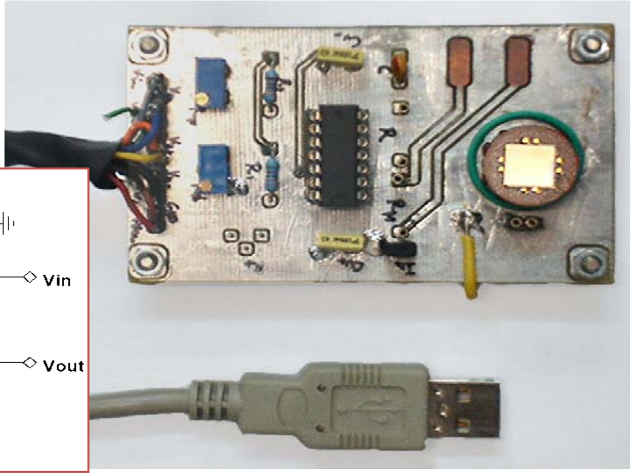
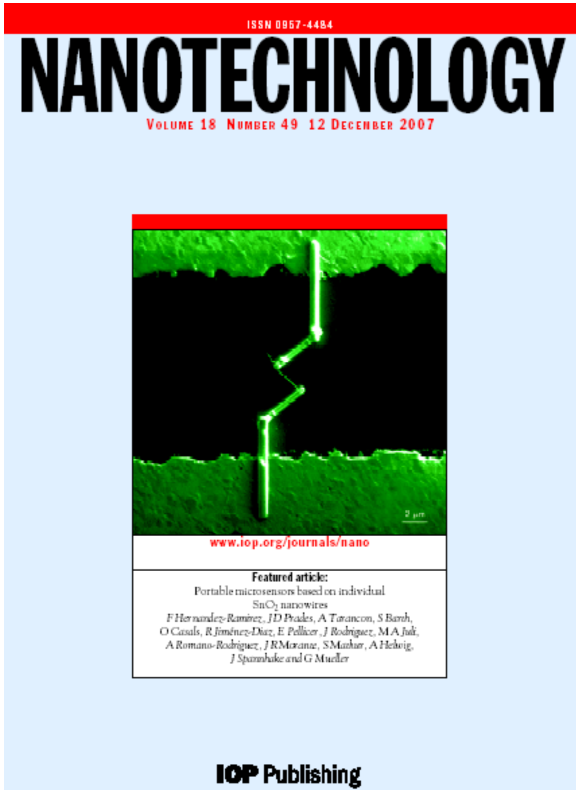
Nanometrology: Portable devices based on a single nanowire. Electrical measurements

application specific hardware

- ✓ Voltage-controlled **low-current** source (pA)
- ✓ **USB** controlled
- ✓ **Low cost** / commercial components







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

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