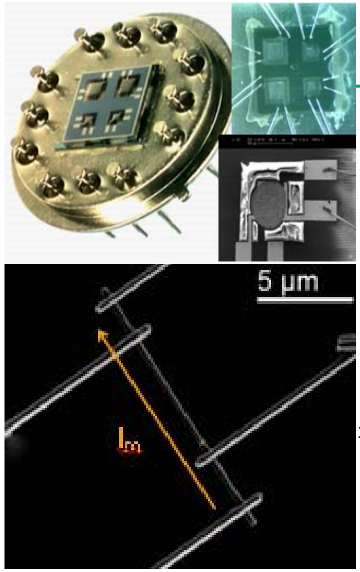

More than 50 years using Metal Oxide materials for optimized Gas Sensor Devices

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More than 50 years using Metal Oxide materials for optimized Gas Sensor Devices

Since 1962 it has been known that metal oxide thin films interact with gaseous components from the surrounding ambient [1].

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

More than 50 years using Metal Oxide materials for optimized Gas Sensor Devices

Nevertheless, in spite of the growing commercial success [9–15], 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/

More than 50 years using Metal Oxide materials for optimized Gas Sensor Devices

It is probable that the major difficulties lie in the structure of the sensing material used itself.

Usually, a nanocrystalline based layer deposited or grown among interdigitized electrodes is used in a real experimental device.

However, this structure prevents detailed studies and analysis from being carried out. Various difficulties exist for it such as surface states of the nanocrystalline material that hide and disguise the molecule interactions and chemical surface reactions, the complex network of grain boundaries existing in the nanocrystalline sensing material that causes charge transfer complexities or the required porosity degree of the non-compact sensing layer that leads to the outstanding question about the gas in and gas out diffusion and about all the kinetic parameters associated with the sensing dynamic.

Furthermore, many basic analyses and studies, like surface analysis, are experimentally performed far away from realistic operation conditions, i.e. vacuum conditions for XPS (x-ray photoelectron spectroscopy), HRTEM (high resolution transmission electron microscopy), EELS (electron energy loses spectroscopy), . . . or the use of a higher target gas concentration than usual for FTIR (Fourier transformed infra-red), Raman, which again prevents fully reliable conclusions on the chemical to electrical transduction mechanisms from being achieved.

In fact, sensor response, attemptable sensitivity, specific selectivity, response and recovery time constants and stability are still, AFTER 50 YEARS, hot topics to be well controlled in the field of resistive solid state gas sensors based on metal oxides

More than 50 years using Metal Oxide materials for optimized Gas Sensor Devices

So, new experimental approaches to achieve deepened knowledge and understanding of the involved mechanisms concerning the chemical to electrical transduction features are still needed.

For this, we are assuming the standard resistive mechanisms [16] but we are also considering new options based on surface ionization of absorbed target molecules [17] enhanced by the implementation of hot surfaces experiencing high external electric fields or for the use of new integrated electrochemical gas sensors [18-19]

The proposed procedure also allows the design and implementation of advanced gas sensor platforms [20] that can work as gas detector devices, although they need to overcome the challenge of feasible nanowire manipulation tools for implementation as industrial methodology [21, 22] in the near future. Moreover, it investigates whether using an individual high quality nanowire, estimated to be an almost perfect monocrystal at the nanoscale level, it is possible to achieve an overall chemical to electrical transduction analysis and, at the same time, it is possible to control, in a much easier way, all the parameters determining the surface chemical reactions taking place at the surface. Therefore, it must allow better knowledge of the individual kinetic parameters and their consequences on the hot sensor characteristics: selectivity, sensitivity and stability [23–27].

[16] Hernandez-Ramırez F, Prades J D, Jımenez-Dıaz R, Fisher T,Romano-Rodr´ıguez A, Mathur S and Morante J R 2009 Phys. Chem. Chem. Phys. 11 Q.20
[17] Hernandez-Ramırez F, Prades J D, Hackner A, Fisher T,M¨uller G, Mathur S and Morante J R 2011 Nanoscale 3 630
[18] A.Tarancon&J.R.Morante et al. Submitted pattent (2013) Fully integrated lambda sensor
[19] A. Tarancon&J.R.Morante et al. Submitted pattent (2013) Fully integrated all solid state electrochemical gas sensors
[20] Hernandez-Ramırez F et al 2007 Nanotechnology 18 495501 2007
[21] Hernandez-Ramırez F, Tarancon A, Casals O, Pellicer E, Rodrıguez J, Romano-Rodrıguez A, Morante J R, Barth Sand Mathur S Phys. Rev. B 76 085429
[22] Hernandez-Ramırez F, Tarancon A, Casals O, Rodrıguez J,Romano-Rodrıguez A and Morante J R 2006 Nanotechnology 17 5577
[23] Hernandez-Ramırez F, Tarancon A, Casals O, Arbiol J,Romano-Rodrıguez A and Morante J R Sensors Actuators B 121 3
[24] Prades J D, Hern´andez-Ram´ırez F, Fischer T, Hoffmann M,M¨uller R, Lopez N, Mathur S and Morante J R 2010 Appl.Phys. Lett. 97 243105
[25] Prades J D, Jimenez-Dıaz R, Hernandez-Ramırez F, Cirera A, Romano-Rodrıguez A and Morante J R 2010 Sensors Actuators B 144 1
[26Prades J D, Jimenez-Dıaz R, Hernandez-Ramirez F, Pan J, Romano-Rodrıguez A,Mathur S and Morante J R 2009 Appl. Phys. Lett.95 053101
[27] Hernandez-Ramırez F, Prades J D, Tarancon A, Barth S,Casals O, J´ımenez-D´ıaz R, Pellicer E, Rodrıguez J,Morante J R and Romano-Rodriıguez A 2008 Adv. Funct.Mater. 18 2990

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More than 50 years using Metal Oxide materials for optimized Gas Sensor Devices

OUTLINE:

- Motivation
- Individual nanowire versus nano particles. Stability.
- Electrical contacts and individual nanowire platform.
- Size effects on the gas sensor response: controlling depletion state
- Self heating phenomenon in nanowires.
- Fully autonomous gas sensor platforms.
- Ultrafast gas sensor platforms: ruling out diffusion and porosity effects.
- Illumination effects on individual nanowires.
- Improving selectivity controlling surface nanowire processes.
- Conclusions.

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Motivation

Commercial solid state gas sensors are currently based on thin/thick layers or micro bead of metal oxide semiconductors deposited onto heaters (ceramic, micro mechanized silicon), 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

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Motivation

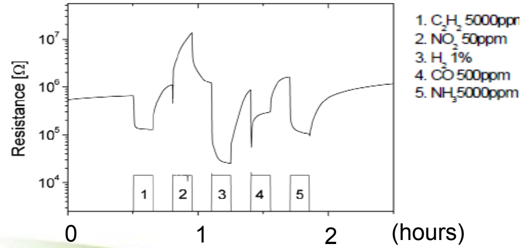
The actual technological approach, besides selectivity problem, presents still some other possible drawbacks:

• (1) relatively high power consumption which restrains or limit their use in portable and/or fully autonomous systems;

•(2) lack of stability and drift problems related to the material degradation;

•(3) not enough fast response and recovery times which become excessively long for many applications.

Consequently, making stable and high quality metal oxide sensors is still a challenging issue.



gas response of a SnO2:Au sensor

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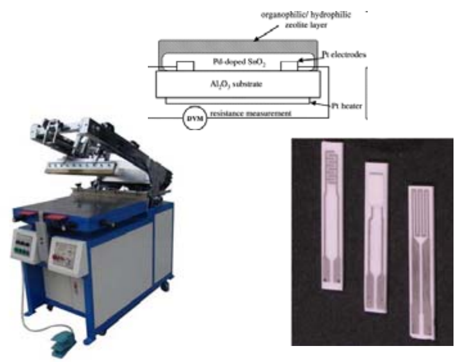
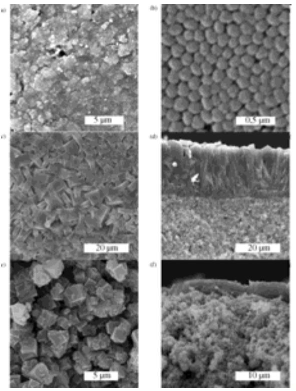
Motivation: (1) Power consumption

sensing platforms

Alumina substrates

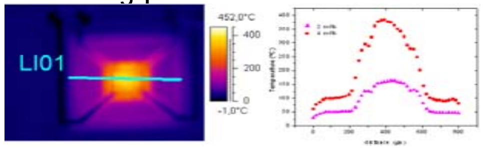
SNB **31**, 1 (1996)
J. Appl. Phys. **90**, 1550 (2001)
Catal. Today **82**, 179(2003)



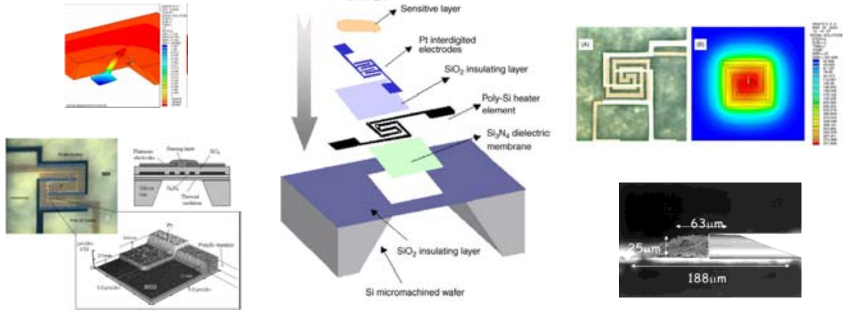


Motivation: (1) Power consumption

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)



Portable and fully autonomous sensors

Energy Source Harvested Power

Vibration/Motion (frequency, amplitude)

Human 4 μW/cm2

Industry 100 μW/cm2

Temperature Difference (Th. gradients)

Human 25 μW/cm2

Industry 1–10 mW/cm2

Light (PV cell efficiency)

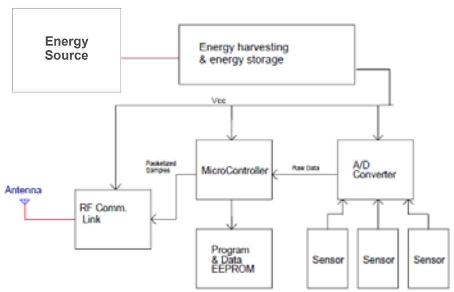
Indoor 10 μW/cm2

Outdoor 10 mW/cm2

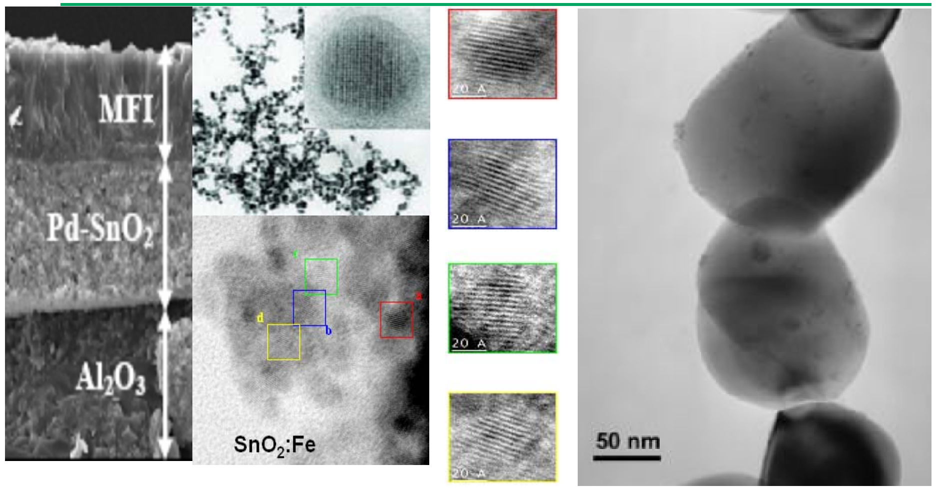
RF (allowed bands)

GSM 0.1 μW/cm2

WiFi 0.001 μW/cm2



Motivation: (2) Stability, drift and degradation



Motivation: (2) Stability, drift and degradation

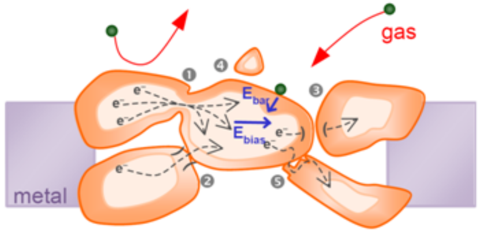
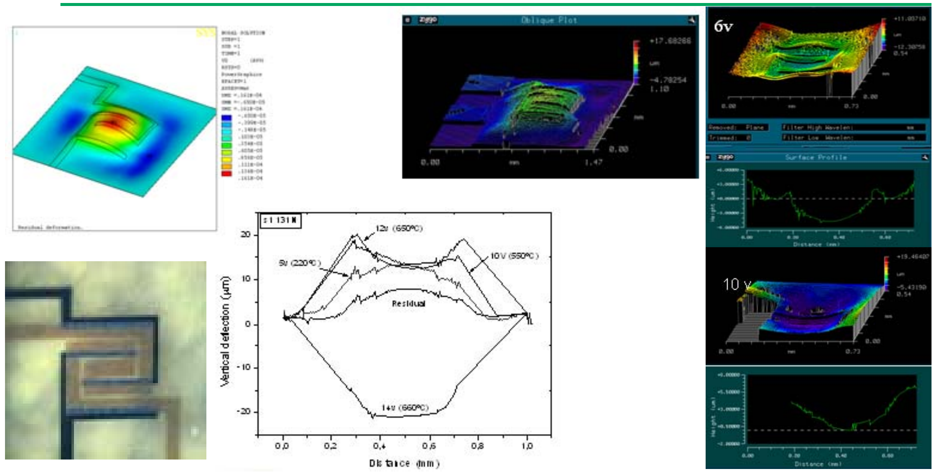


Diagram illustrating different types of necks in polycrystalline metal oxide matrices derived from the random nature of the layer. ❶ & ❷ Thick and thin necks between grains: the thicker the neck, the easier the electron transfer. ❸ & ❹ Intergrain boundary without material continuity: if the intergrain distances is short enough, electron transfer will take place by tunnel-assisted mechanisms. ❺ Non homogeneous intergrain interface. In this scenario the electric field that causes the band bending near the surface due to the gas interaction (Ebar) and the electrical field externally applied to perform the conductometric measurements (Ebias) are not necessarily orthogonal.

PHYSICAL CHEMISTRY CHEMICAL PHYSICS 11 ; 7105,(2009)

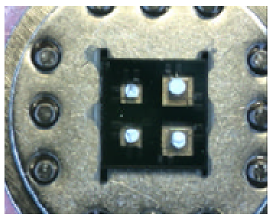
Motivation: (2) Stability, drift and degradation

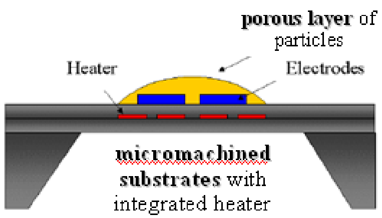


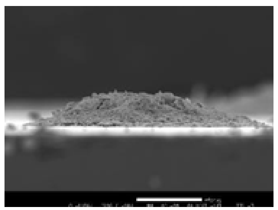
. *Micromech. Microeng.* **13**, 548 (2003)
SNB **114**, 826 (2006)
SNB **114**, 881 (2006)

Motivation: (3) Response and Recovery Times, too many experimental problems

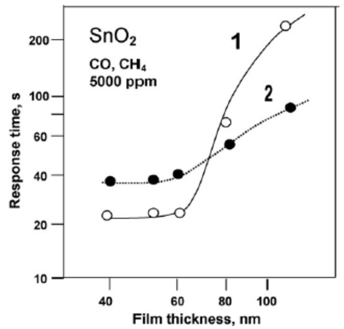
- Diffusion test chamber time: Geometrical parameter, Flow and pressure of the injected gas.
- Diffusion through the sensing layer: geometrical parameters of the layer, essentially its thickness, porous degree, porous size, etc., …
- Chemical interaction between the gas molecule and the surface of the solid sensing material: Kinetic of the chemical reaction.





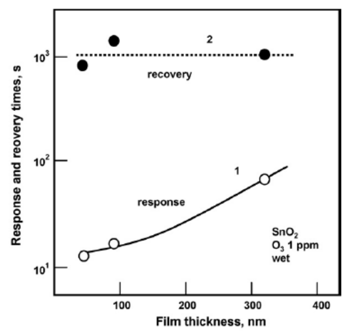


Preliminary experimental studies on time constants



(1)CO (T_{oper} = 340 ºC)
(2) CH4 (T_{oper} = 430 ºC)

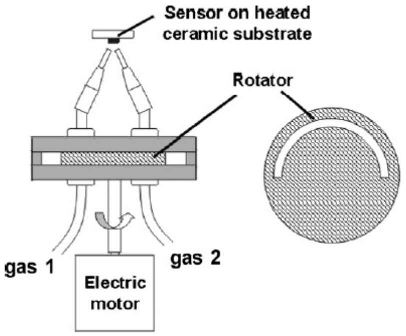
G. Korotchenkov, V. Brynzari, S. Dmitriev, J. Mater. Sci. Eng. B 63 (3) (1999) 195–204



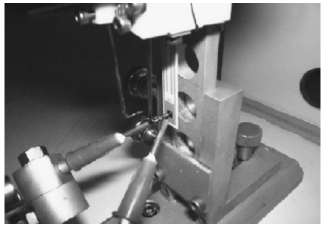
Ozone detection at T_{oper} = 220 ◦C in a wet atmosphere

G. Korotcenkov, B.K. Cho / Sensors and Actuators B *(2009)*

Moving gas outlet technique



A. Helwig et al. / Sensors and Actuators B 126 (2007) 174–180

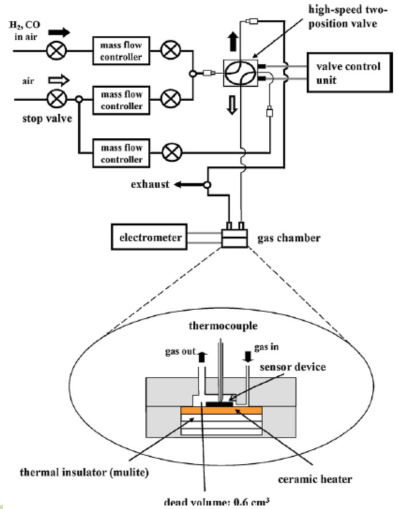


Moving gas outlet set-up. The rotating wheel with the half-circular opening in the centre produces a step function change between gas 1 and gas 2 at the sensor surface.

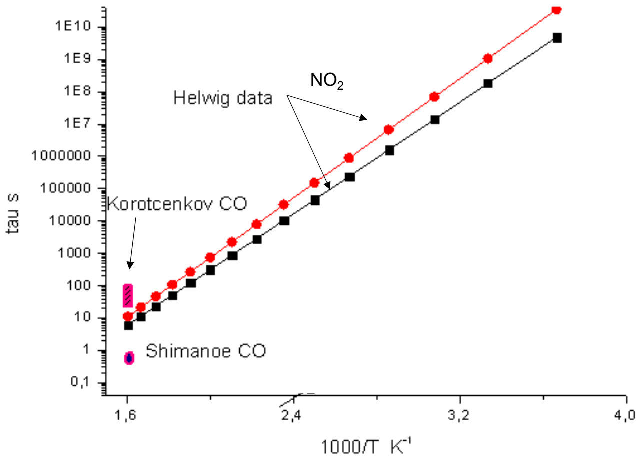
High gas flow injection system

gas flow apparatus equipped with a high-speed gas-switching valve operative at a rate of 30ms

T. Kida et al. / Sensors and Actuators B 134 (2008) 928–933

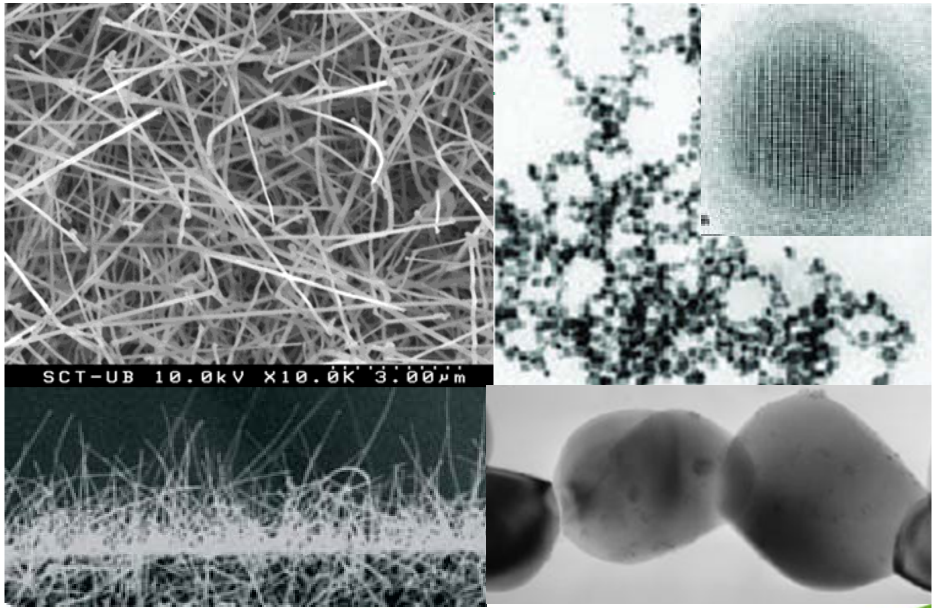


Data base information about reported time constants



Individual nanowire platforms

Individual nanowire versus nano particles.
Stability



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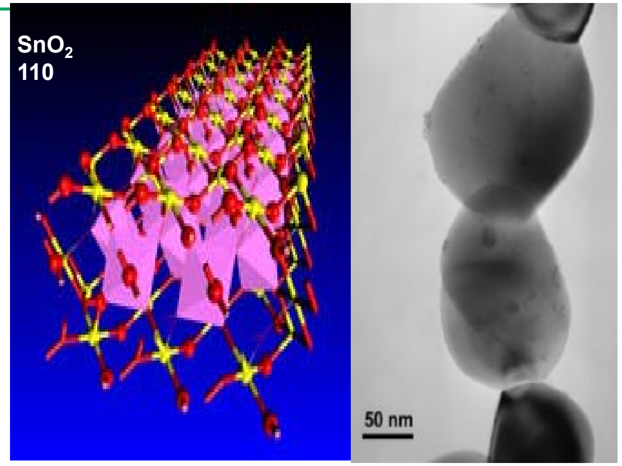
Ultimate limits? New properties?

Nano structures:

What happens by considering an individual almost perfect nano structure, like a single nanowire instead a multiple association of nanoparticles or nanowires with many boundaries problems determining the electrical behavior?



Furthermore, can the nanostructure size determine the final sensing behavior?

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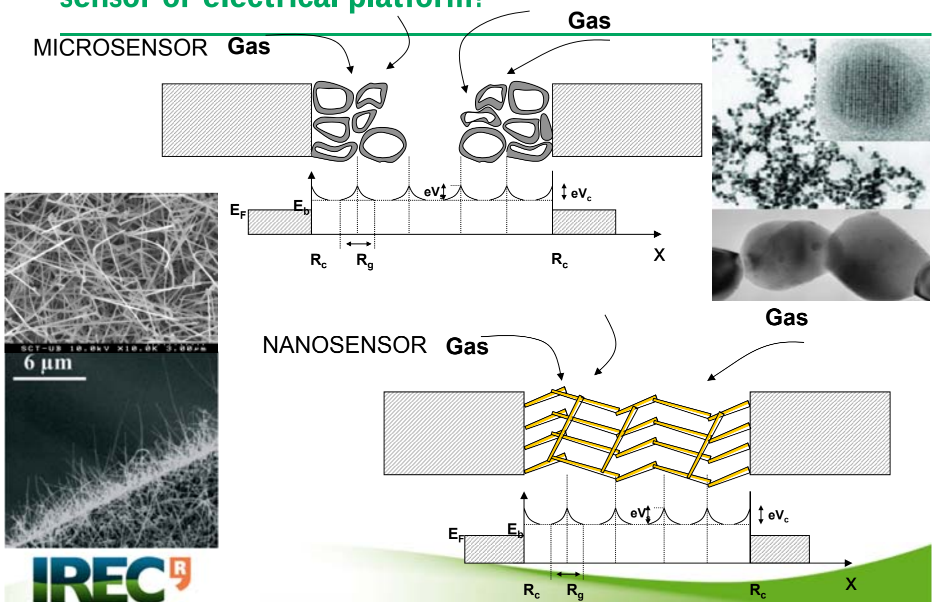
Nanometrology: Many or only a single nanowire as sensor or electrical platform?



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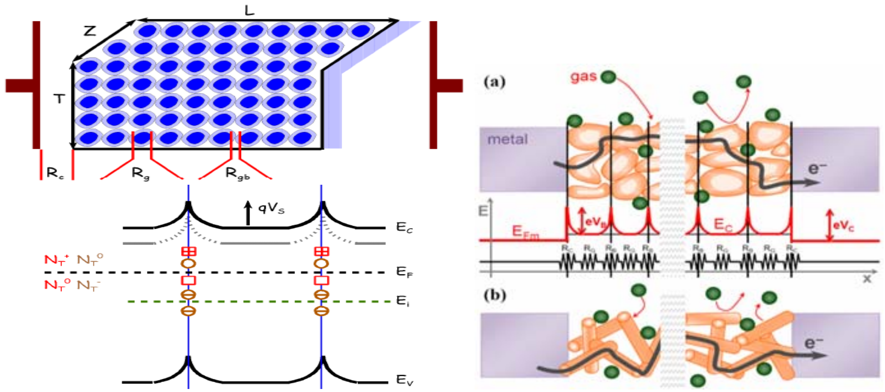
Nanometrology: Many or only a single nanowire as electrical platform for gas sensing?



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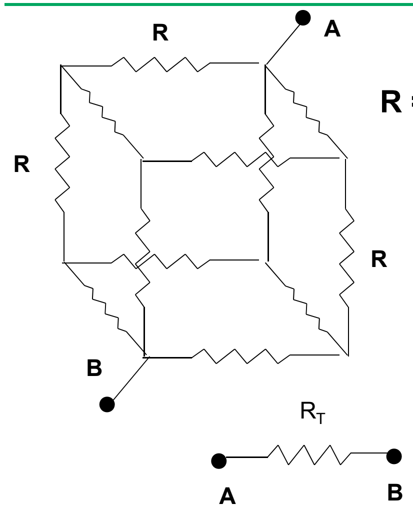
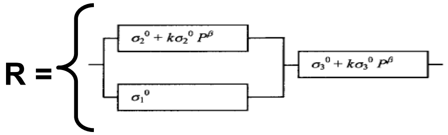
Nanometrology: Many or only a single nanowire as sensor?



Elemental cell in a 3D network



$$R_T = (5/6) \cdot R$$

$$(R_T + \Delta R_T) = (5/6) \cdot (R + \delta R)$$

$$(R_T + \Delta R_T) = (5/6) \cdot R + (5/6) \cdot \delta R$$

$$\Delta R_T / R_T = (5/6) \cdot (\delta R / R) \cdot (6/5)$$

$$\Delta R_T / R_T = (\delta R / R)$$

http://www.ilovephysics.com/forum/p1751-2006-05-07-17:58:49.html

http://mathforum.org/library/drmath/view/65234.html

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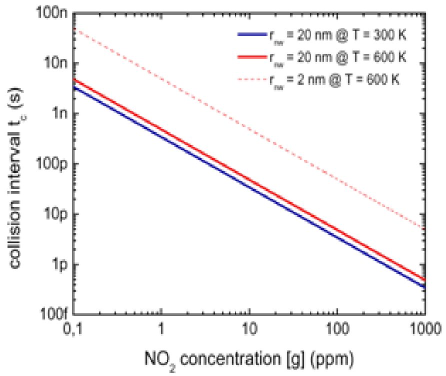

Collision interval *tc* as function of gas concentration (NO2).

Different nanowire's radii and working temperatures are considered Ln=1 micron

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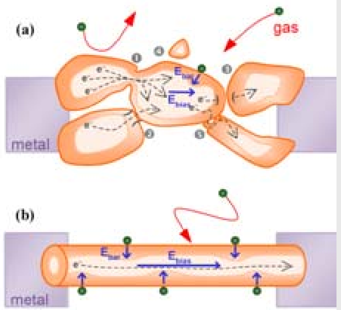
Nano particles versus Nanowires.

PHYSICAL CHEMISTRY CHEMICAL PHYSICS 11 ; 7105,(2009)



(a) Diagram illustrating different types of necks in polycrystalline metal oxide matrices derived from the random nature of the layer. ❶ & ❷ Thick and thin necks between grains: the thicker the neck, the easier the electron transfer. ❸ & ❹ Intergrain boundary without material continuity: if the intergrain distances is short enough, electron transfer will take place by tunnel-assisted mechanisms. ❺ Non homogeneous intergrain interface. In this scenario the electric field that causes the band bending near the surface due to the gas interaction (E_{bar}) and the electrical field externally applied to perform the conductometric measurements (E_{bias}) are not necessarily orthogonal. (b) Diagram illustrating the gas interaction in individual nanowires: any intergrain necks or boundaries are considered. Moreover , E_{bar} and E_{bias} fields are always orthogonal.

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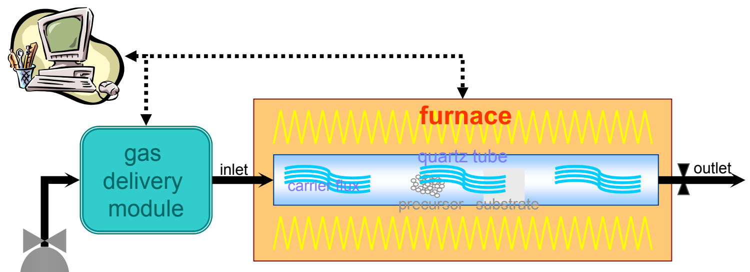
Synthesis: CVD equipment



ZnO nanowires recipe:

Precursor powder:	50g $ZnO_{(99.99\%)}$ + 250g graphite $powder_{(crystalline,\ 99\%)}$
Substrate:	Au/SiO_2
Carrier gas:	$Ar_{(99,999\%)}$
Flux rate:	400ml/min
Pressure:	760torr
Temperature:	900ºC
Time:	~30min

CVD specifications:

Chamber:	quartz tube (Ø5cm, L60cm)
Gas delivery module:	4 MFC 20 to 10000sccm
Pressure control:	50mtorr to atm
Furnace:	Max.Temp 1200ºC, 3 independent heating zones

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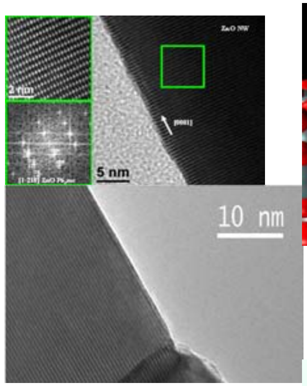
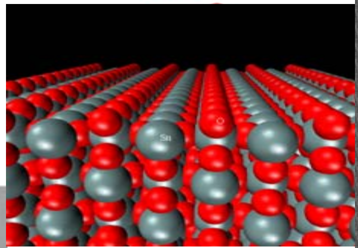
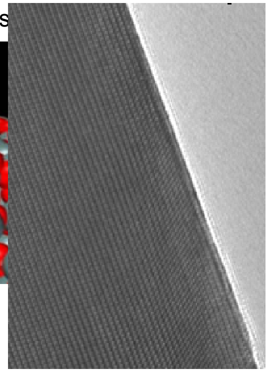
Stability

- ✓ Nanowires (and other 1D particles) are single-crystalline materials…
- ✓ … with well defined and stable surfaces exposed to gas







Nanotechnology **17**, 495501 (2006)

All this favors the stability and reversibility of the response

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Electrical contacts and individual nanowire platforms

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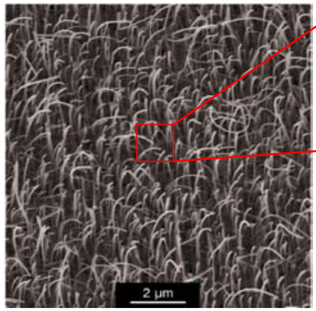
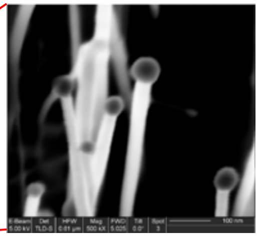
Deposition

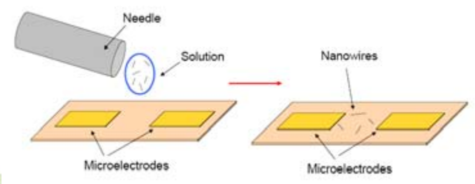
Nanowires are dispersed over a substrate with pre-patterned microelectrodes:

Adv. Funct. Mater. 10.1002/adfm.200701191



SnO_2 Nanowires





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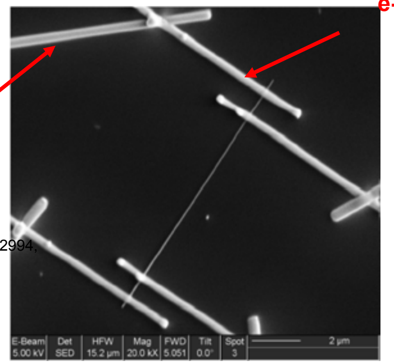
Individual nanowire platforms

Nanofabrication: botom-up approach

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

Nanotechnology **17**, 5577 (2006)



Nanotechnology, 18(49) 2007
Advanced Functional Materials 18,2990-2994 (2008)

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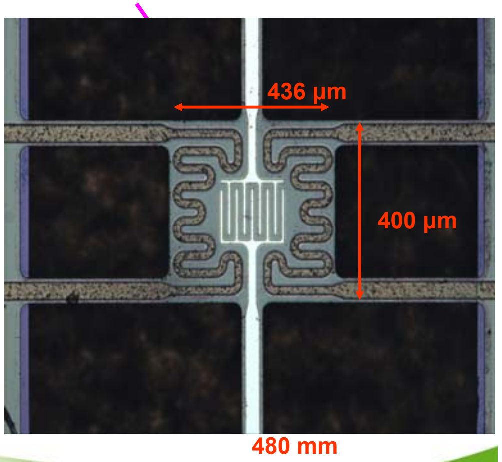
Individual nanowire platforms

Integration into Micromembranes

- Micromembranes with microheaters
- Nanowires transferred to these chips
- Microdropping / nanomanipulation
- SnO_2 and ZnO nanowires
- FIB Strata DB 235 FEI
- e – beam & i – beam Pt depositions
- Gas sensors and UV photodetectors



Nanotechnology 18 No 49 (2007) 495501

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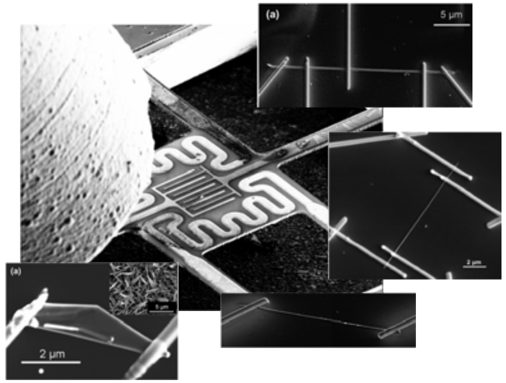
Electrical contacts on individual nanowires

Sensing platforms based on **individual nanowires**

Nanofabrication: Focused Ion Beam (FIB) *Nanotechnology* **17**, 5577 (2006)



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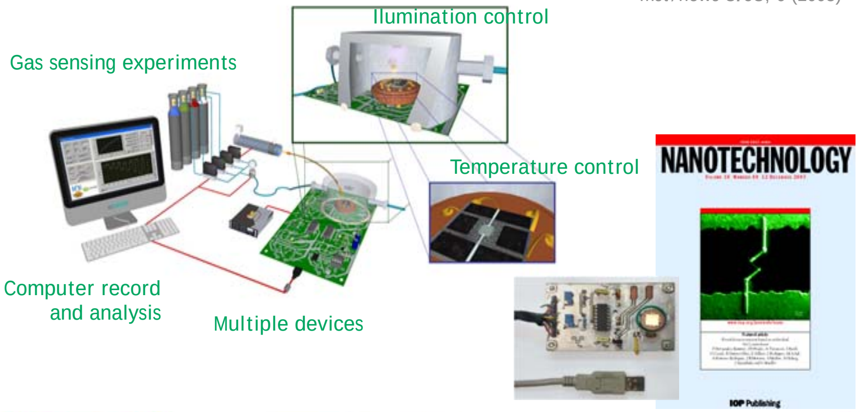
Advanced test system

Sensing platforms based on **individual nanowires**

Electrical characterization

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



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Size effects on the gas sensor response: fully depletion state

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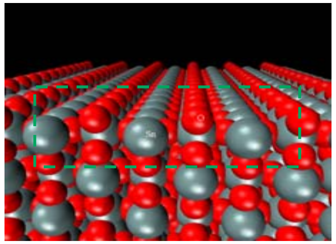
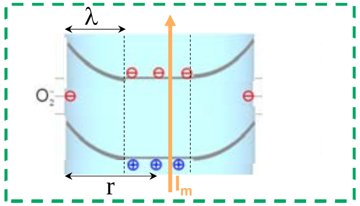
Sensor response

- ✓ Gas sensing **is** a surface effect
- ✓ Chemicals trap charges at the surface ⇒ band bending near the surface metal ⇒ electrical resistance modulation

Sens. Actuators B **121**, 3 (2007)





- ✓ The higher the surface-to-volume ratio the higher the response

Good for nano!

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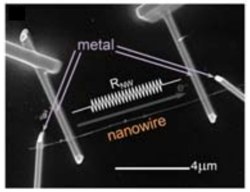
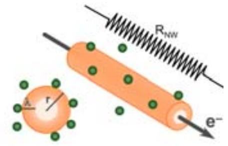
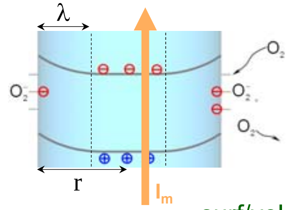
Sensor response



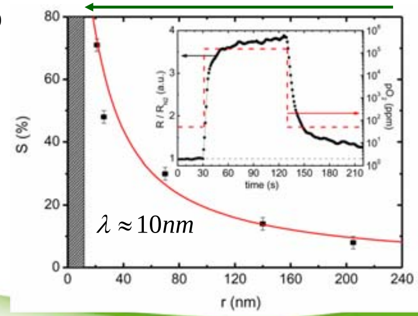




$$S(\%)=\left[\frac{R_{NW-SA}-R_{NW-N_2}}{R_{NW-SA}}\right]\cdot 100=\left[\frac{r^2-(r-\lambda)^2}{r^2}\right]\cdot 100$$

Adv. Funct. Mater. **18**, 2990 (2008)

- ✓ Individual nanowires with shrinking diameter
- ✓ The thinner the nanowire the higher the response



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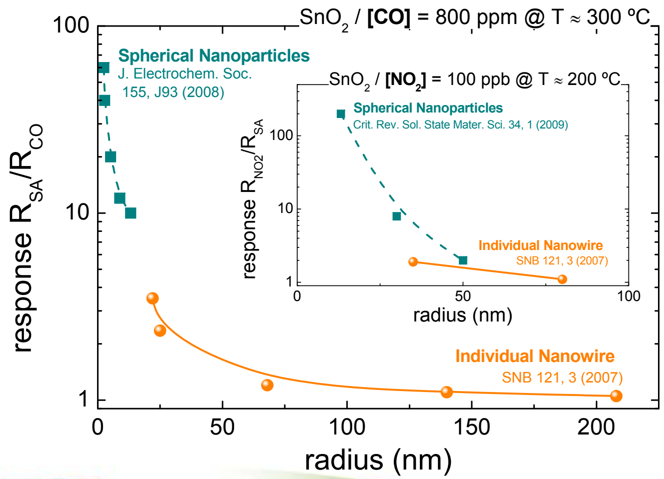
Sensor response versus crystal size



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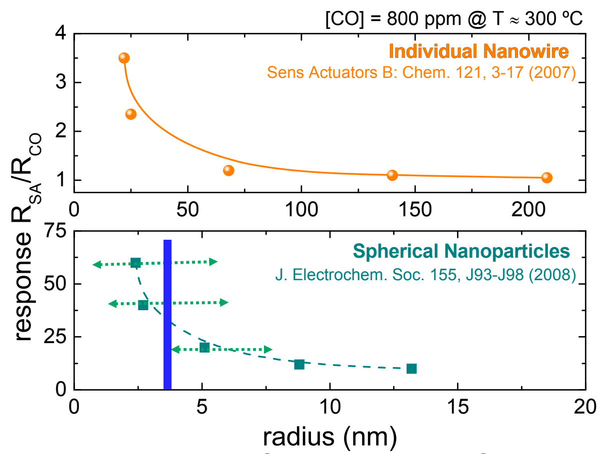
Details of the influence of the crystal grain on the sensor response

JOURNAL OF SENSORS, (2009) 783675



Full shrinkage of the nanograin?

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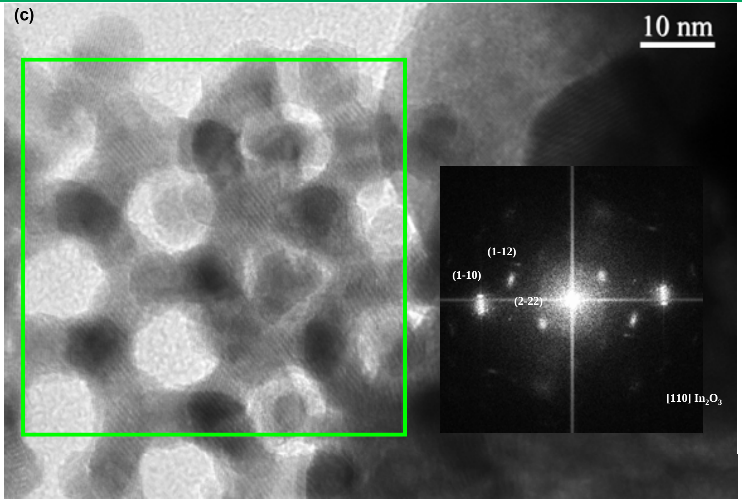
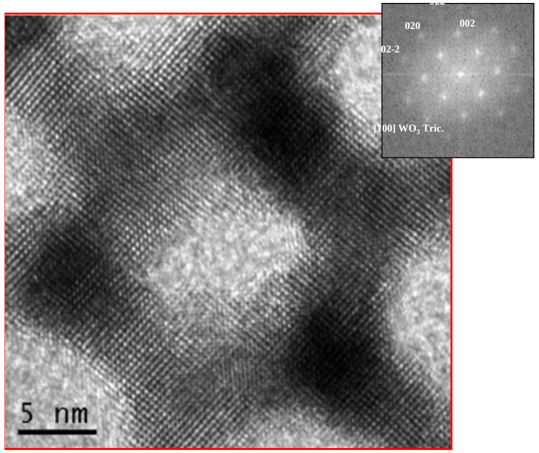
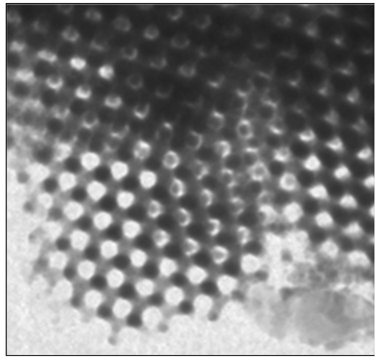
Mesoporous replica In2O3



In2O3

Mesoporous replica WO3





WO3 Kit-6

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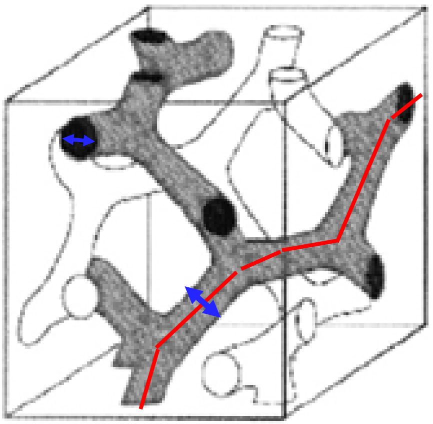
Conduction channel shrinkage



Conditions for a maximum ΔR?

In2O3 7nm

WO3 5nm

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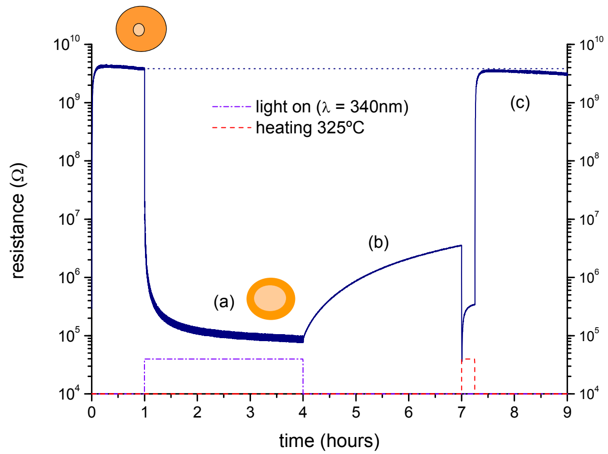
Resistance modification



In2O3

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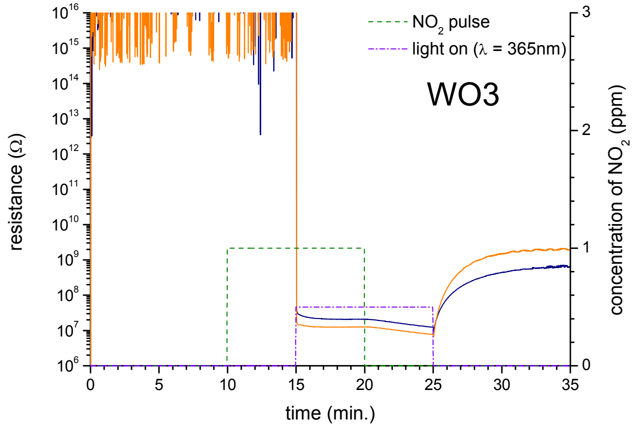
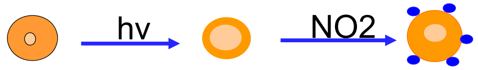
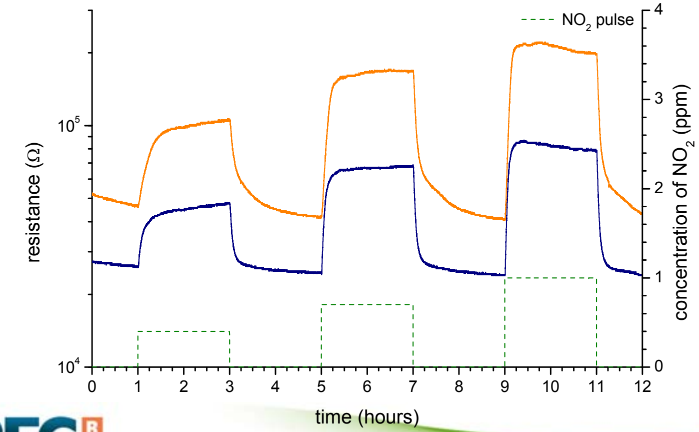
Resistance modification



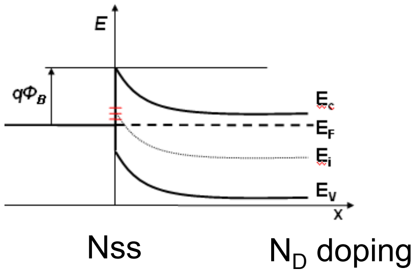
Under illumination at room temperature oxidant molecules



WO3



Parameters affecting surface depletion



N_D

Nss

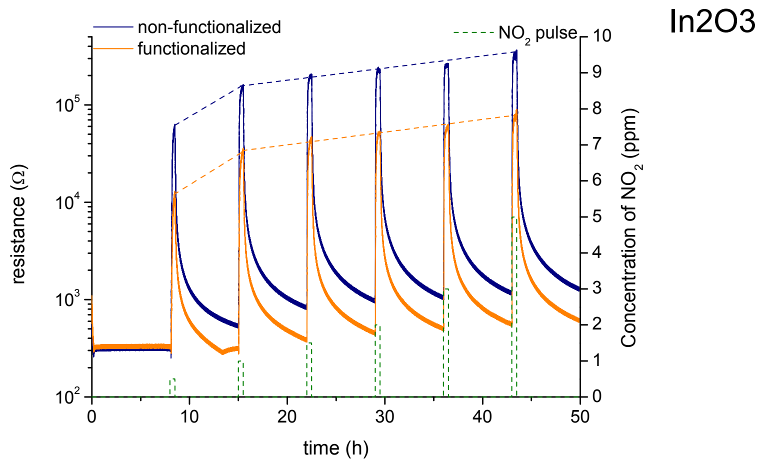
Option: Modification of Nss by chemical suface treatment (functionalization)

Surface chemical treatment (functionalization)

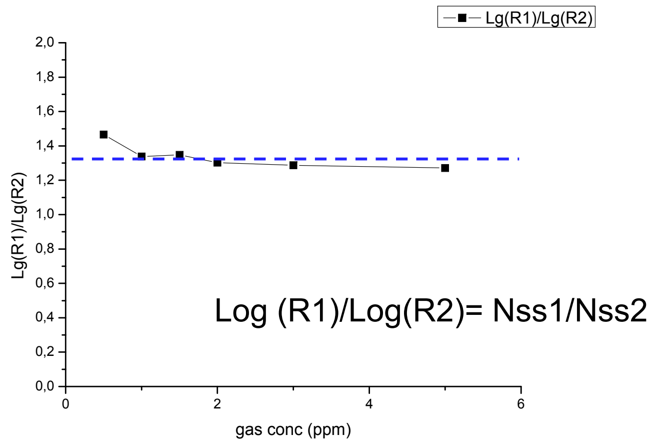
Some samples were functionalized with diethyl 3-aminopropylphosphonate .

Since P-O-M bonds are more thermodynamically stable than Si-O-M bonds, phosphonate blocks the surface sites in the right direction. In addition to this, the reaction of metal oxides with phosphonate is easier even in the absence of hydroxyl groups

Room Temperature Sensor Response



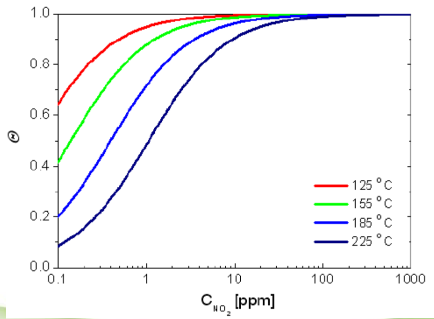
Effects of the surface state density modification



Adsorption Desorption kinetic effcts: Surface coverage at room temperature

$$\frac{d\Theta}{dt} = k_{ads} p_{gas}(1-\Theta) - k_{des}\Theta$$

$$\Theta = \frac{kP_{gas}}{(1+kP_{gas})} \quad \text{with } k = \frac{k_{ads}}{k_{des}} = \frac{k_{ads,0}}{k_{des,0}} \cdot \exp\{\Delta H_{chem.} / kT\}$$

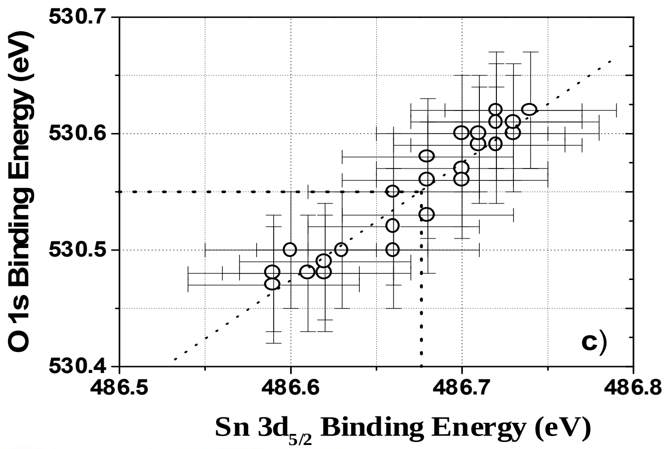


Additives effects

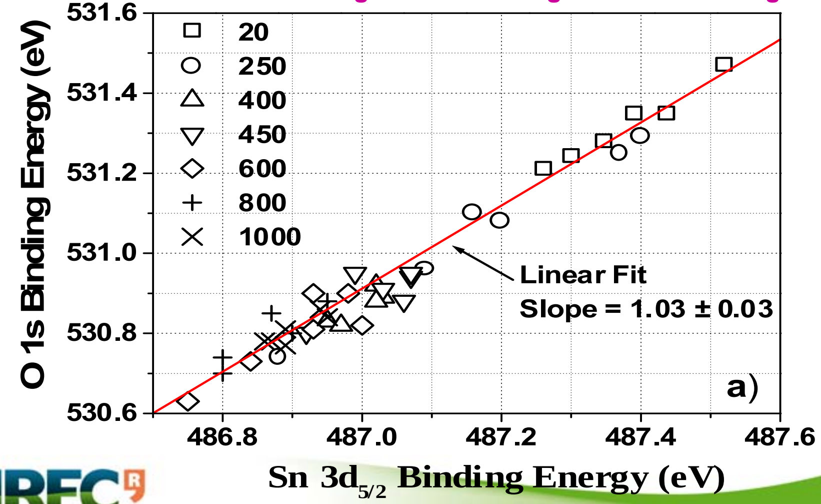
Usually the use of additives looking for catalytic effects is applied.

However, few detailed analysis at the surface are performed and mechanisms and data are not discussed.

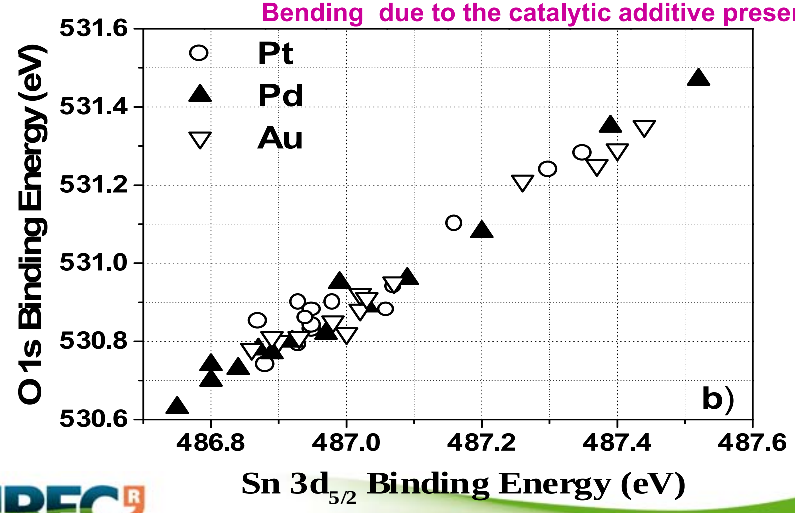
It means a lot of effects at the surface and usually surface analysis are difficults

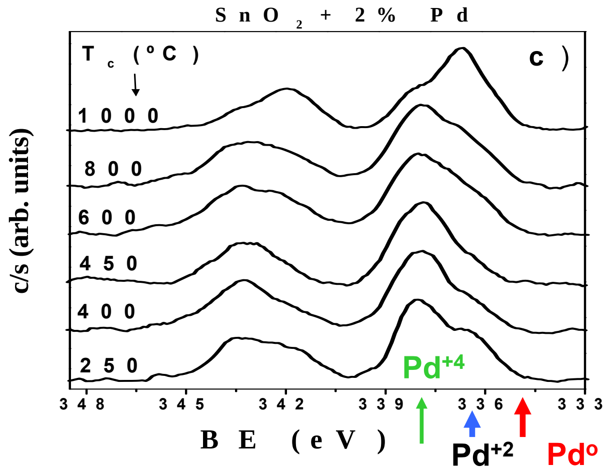


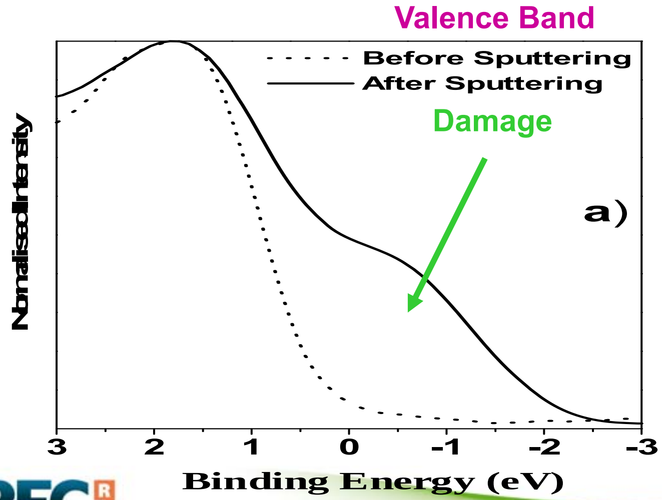
Fermi Level shift at the grain surface region:Band bending



Bending due to the catalytic additive presence







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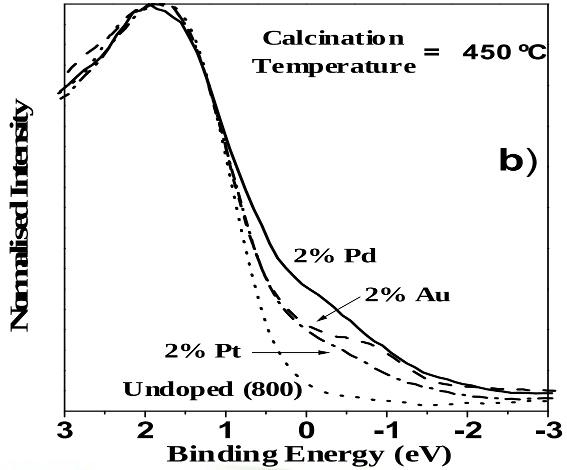

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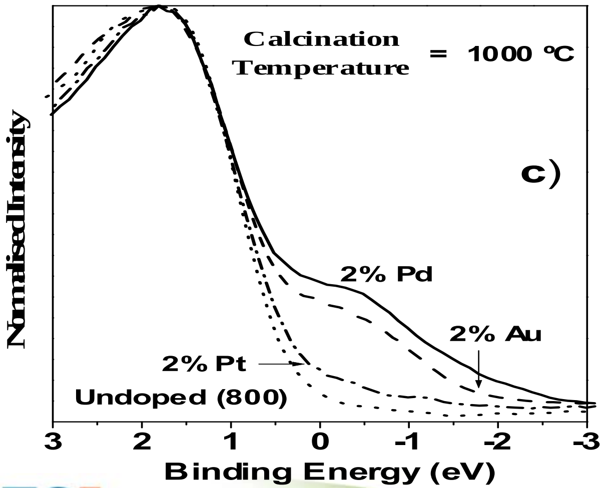

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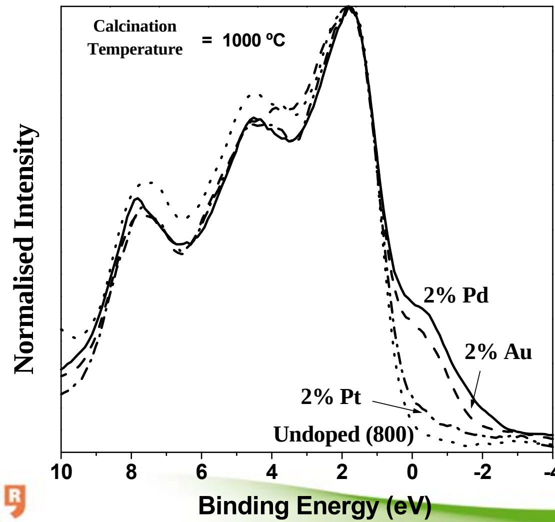

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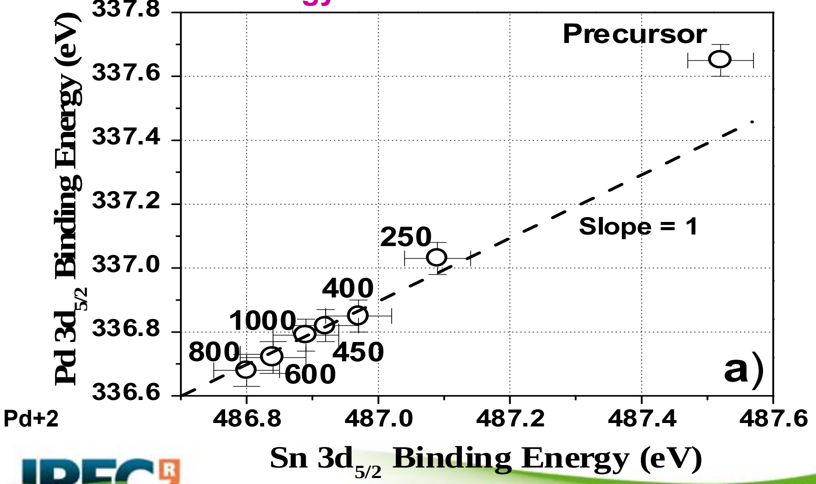
Pd^{+2} energy level follows Tin dioxide lattice energy



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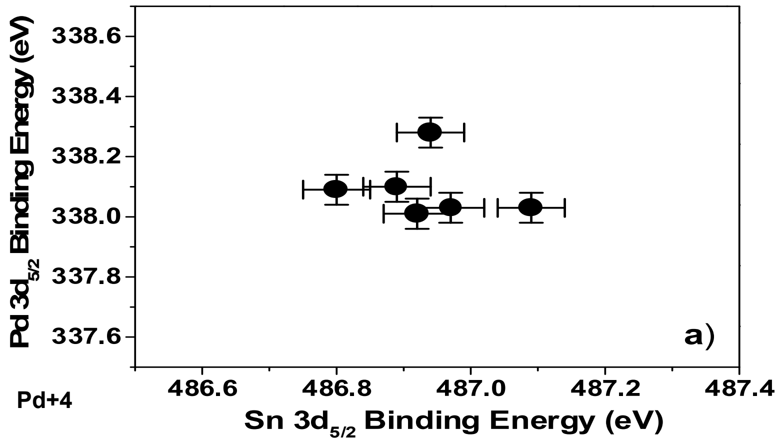
Pd^{+4} level energy seems not follow SnO_2 lattice energy



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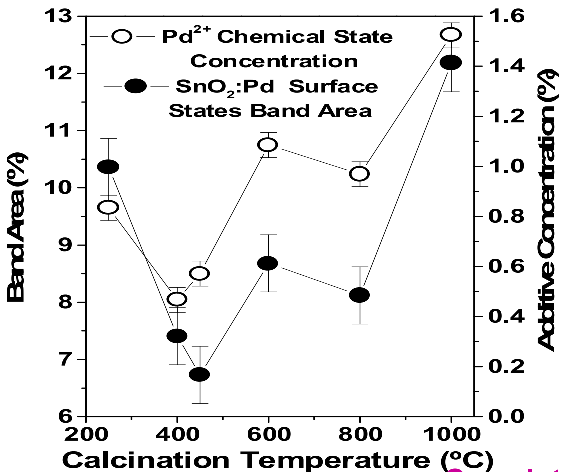

Correlation between Pd^{+2} and Surface States Band Area

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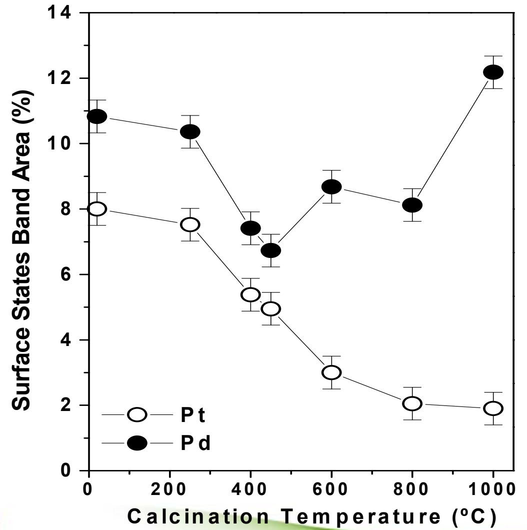

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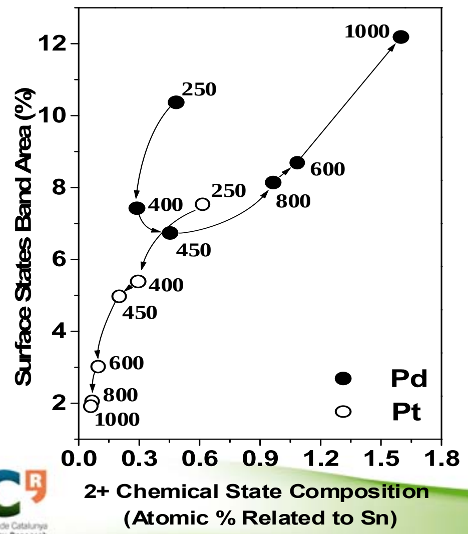
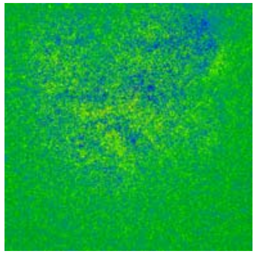
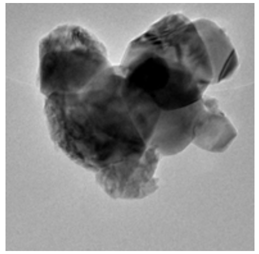
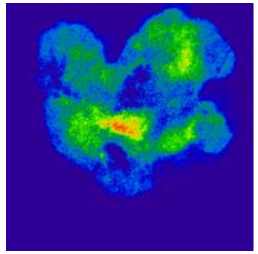
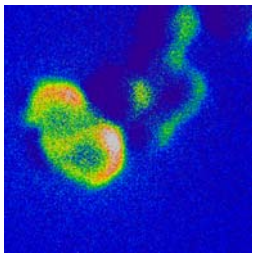
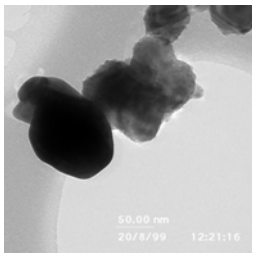


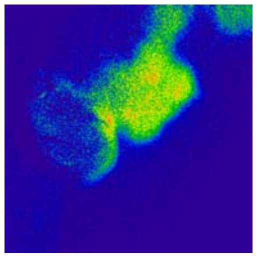

GIF Pt map


TEM micrograph


GIF Sn map


GIF Au map


TEM micrograph


GIF Sn map

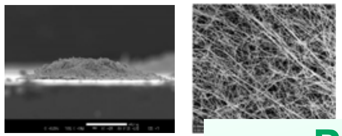
Self heating phenomenon in nanowires

Power consumption

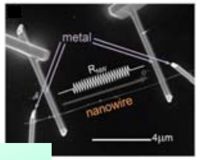
✓ **Two steps downscaling**

Appl. Phys. Lett. **93**, 123110 (2008)

1) Sensing element



porous layers, bunch o…

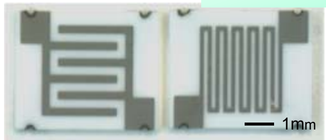


…dual nanowire

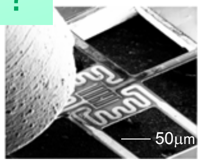
P ~ 10 mW

Can we do it better?

2) Heating eleme…



millimeters scale



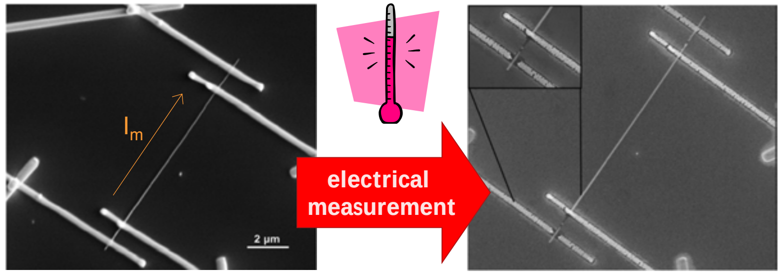
microelectronics

Self-heating approach

Self-heating in nanowires

Concept

Sens. Actuators B **118**, 198 (2006)
Phys. Rev. B **76**, 085429 (2007)
Appl. Phys. Lett. **93**, 123110 (2008)
MRS Spring Meeting (2005)



✓ Local **self-heating** in nanowire based devices threatens their stability

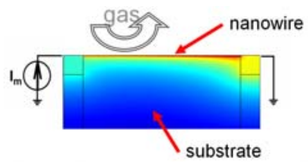
✓ **Low current values** required to avoid uncontrolled damage

Sens. Actuators B **118**, 198 (2006)
Phys. Rev. B **76**, 085429 (2007)
Appl. Phys. Lett. **93**, 123110 (2008

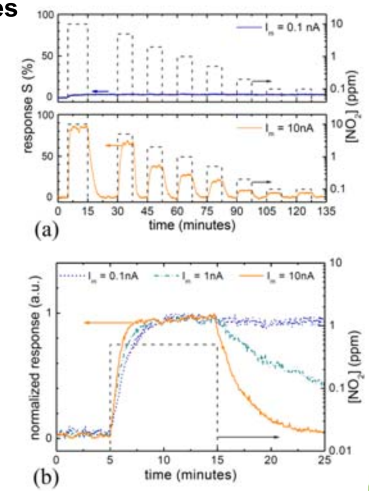
Integrated heat source?

Power consumption

Sensors based on Self-heated nanowires



Appl. Phys. Lett. **93**, 123110 (2008)



✓At very low probing current (I_m)
… poor response
… no recovery

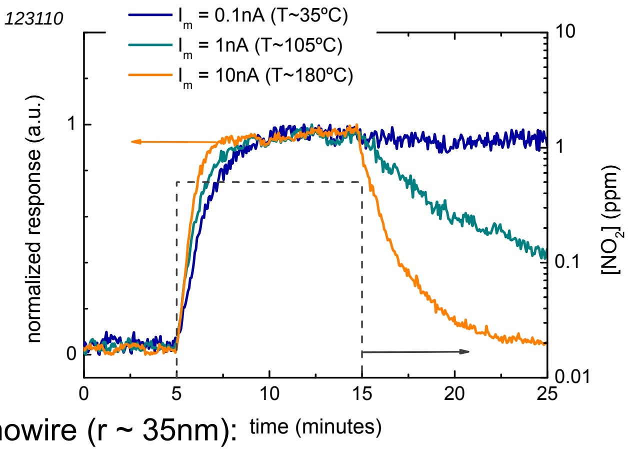
✓At higher probing current
… better response
… faster recovery

✓ Similar to the effect of an external heater

It works!

Experimental boundaries: Self-heating

Appl. Phys. Lett. 93, 123110 (2008)



SnO_2 nanowire (r ~ 35nm):

Self-heating also ease desorption and accelerate recovery after gas pulse

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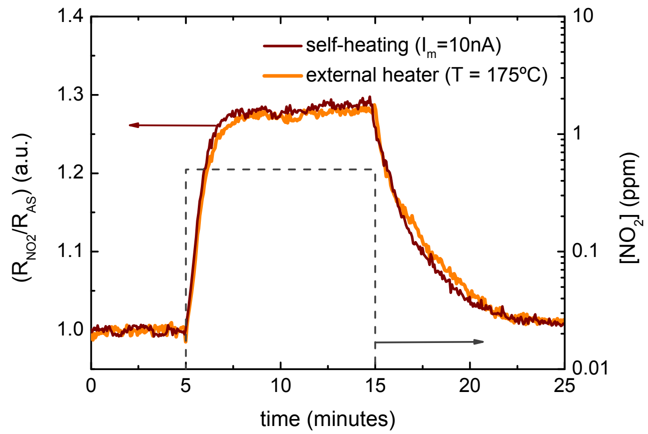
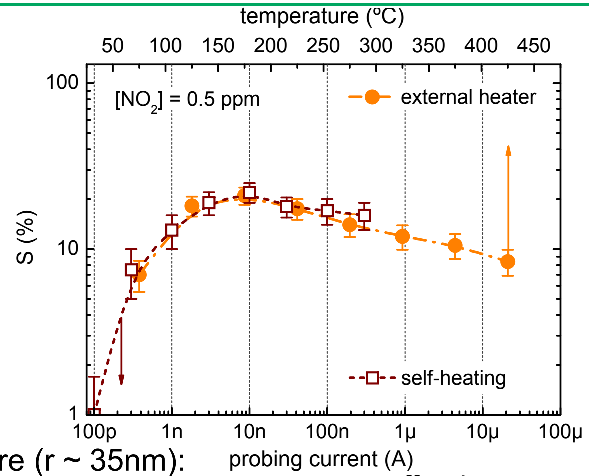
Experimental boundaries: Self-heating



SnO$_2$ nanowire (r ~ 35nm): *Appl. Phys. Lett. 93, 123110 (2008)*
SENSORS AND. ACTUATORS B: 140 (2009) 337

Experimental boundaries: Self-heating

Appl. Phys. Lett. 93, 123110 (2008)



SnO$_2$ nanowire (r ~ 35nm):
Equivalent response to gases may serve to effective temperature due to self-heating

Power consumption

Ultra-low power gas sensors

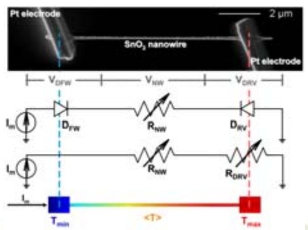
Appl. Phys. Lett. **93**, 123110 (2008)
Int. J. Nanotechnol. submitted (2008)

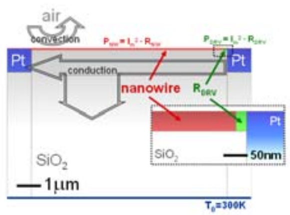
✓ The nanowire itself and the rectifying contacts contribute to self-heating.

✓ Preliminary FEM simulations: important role of the contacts.

"very low power consumption: less than 20µW"

(measurement AND HEATING included!!!)





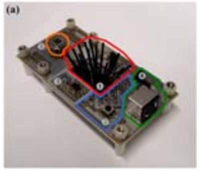
Sens. Actuators B **118**, 198 (2006)
Phys. Rev. B **76**, 085429 (2007)

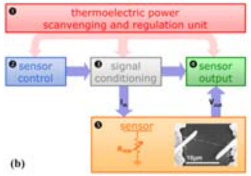
Fully autonomous gas sensor platforms

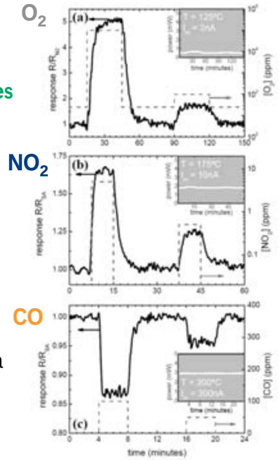
Fully autonomous gas sensor platforms

Sens. Actuators B **in press** (2009)
Spanish patent No.P200900334

- ✓ **Self-heating enables** power consumptions of only a **few tens of microwatts**:
  - ⇒ **in range with** current **energy harvesting technologies**

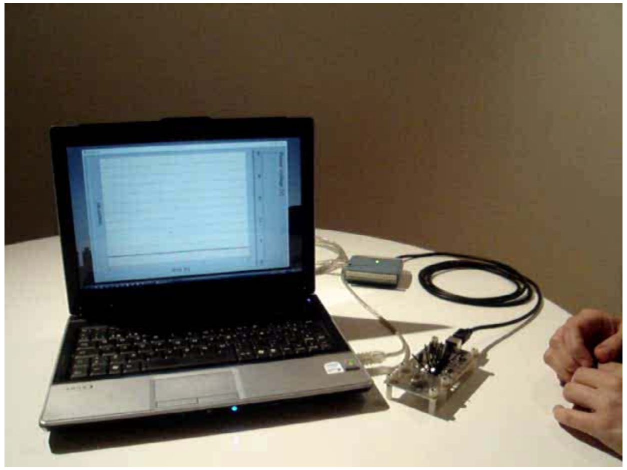






- ✓ Demonstrator: Individual nanowire coupled to a **thermoelectric microgenerator**
- ✓ "Smart dust" spot operates with **only ΔT ~ 12ºC**

Fully autonomous system



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Ultra fast gas sensor platforms: ruling out diffusion and porosity effects

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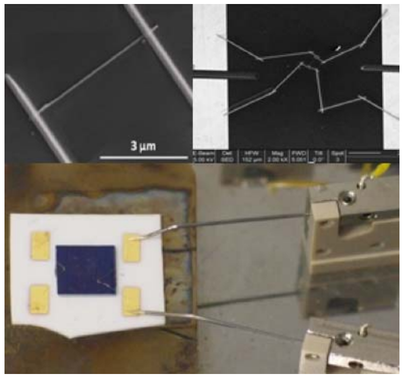

Details of the electrical connections performed in a single nanowire by focused ion beam (FIB) using metallized pads on a supporting substrate and an external micromanipulator tip for connecting the external measurement circuit. The internal and external pads are wire bonded. The top left shows two electrical contacts performed in a single nanowire. The top right shows the area between the four electrical contacts and the previously prepared pads needed to bring the electrical signal from the nanowire to the macroscopic world.

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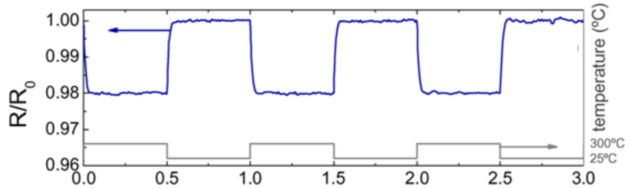
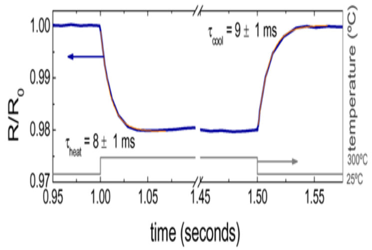
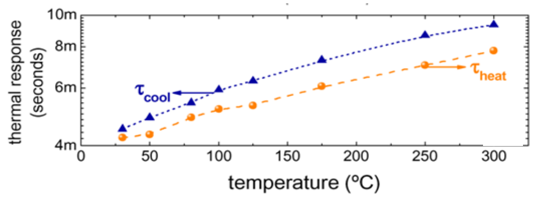
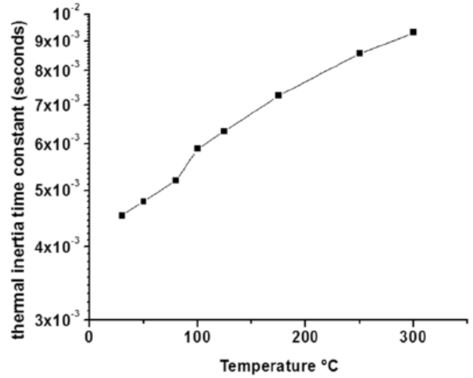
Thermal inertia: thermal time constants



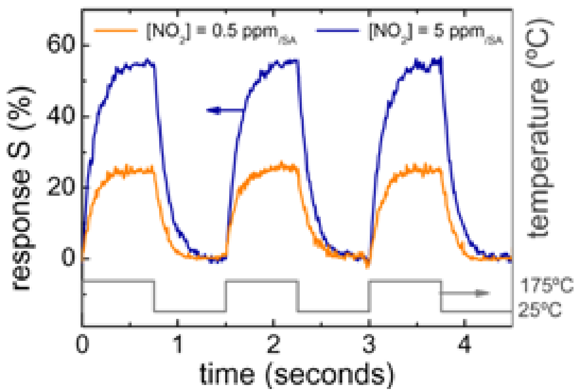




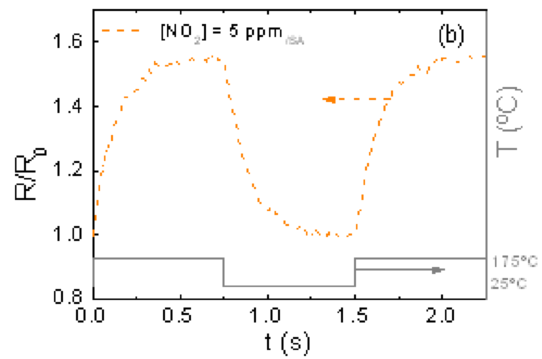


Thermal inertia response time constants in seconds deduced from the resistance signal when a current pulse is applied.

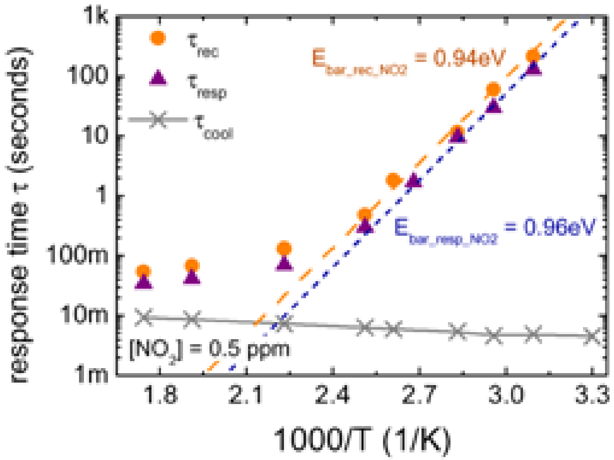
NO_2 analysis



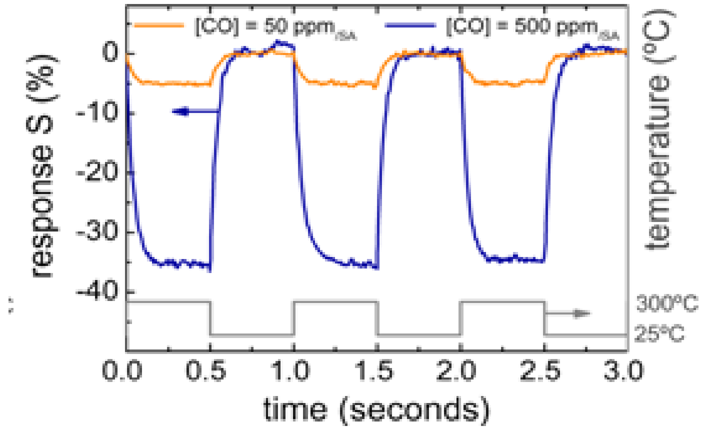
NO_2 analysis



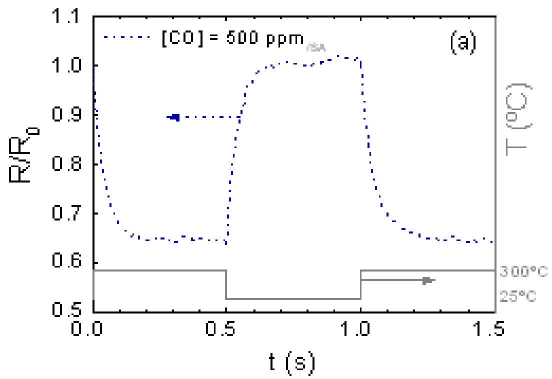
Summary of the NO_2 analysis



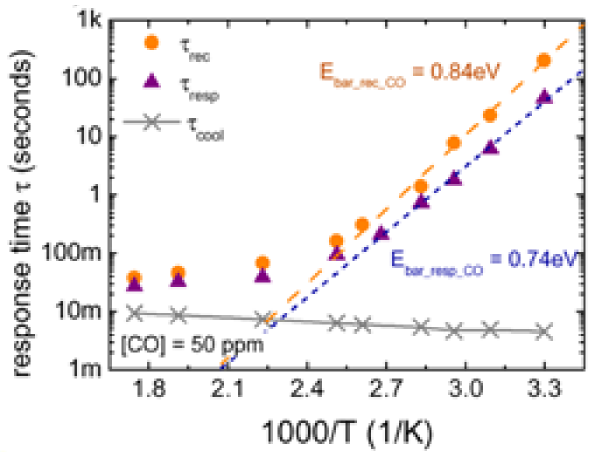
CO analysis

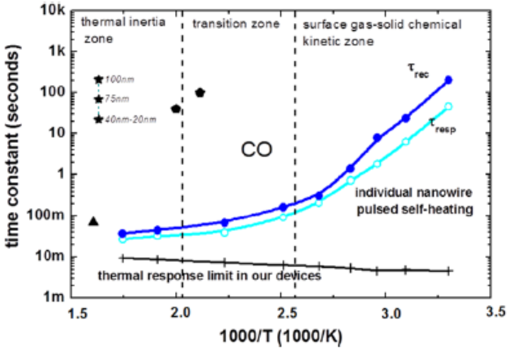


CO analysis



Summary of the CO analysis

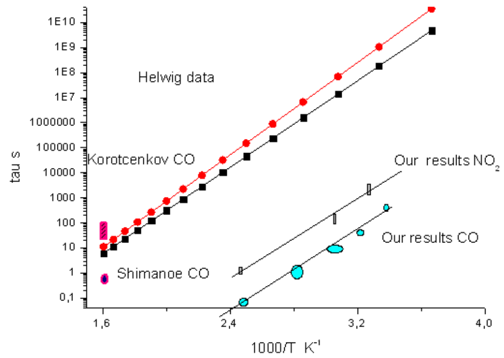




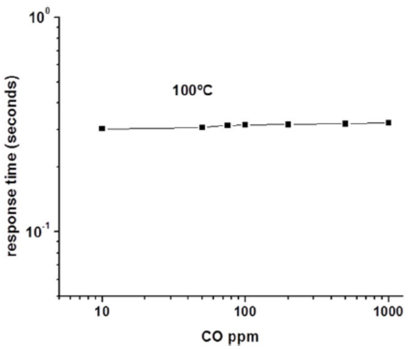
Response time constants as a function of the concentration of carbon monoxide at temperatures above 273 K.. The CO concentration is 500 ppm. The stars correspond to different thin film thicknesses shown in the figure [55]; the triangle [56] and polygon [57, 58] symbols are data from previously published papers.

[55] Korotchenkov G, Brynzari V and Dmitriev S 1999 Mater. Sci.Eng. B 63 195
[56] Kida T, Kuroiwa T, Yuasa M, Shimanoe K and Yamazoe N 2008 Sensors Actuators B 134 928
[57] Kolmakov A, Zhang Y, Cheng G and Moskovits M 2003 Adv.Mater. 15 997
[58] Lopez N, Prades J D, Hernandez-Ramırez F, Morante J R, Pan J and Mathur S 2010 Phys. Chem. Chem. Phys. 12 2401

Summary of sensing time constants

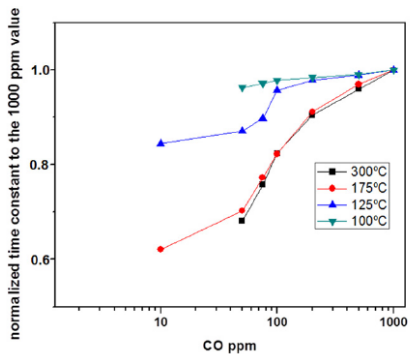


Molecular and monoatomic oxygen



Time constant at 100♬C for different CO concentrations from 10 to 1000 ppm. No appreciable or significant dependence on the CO concentration is shown

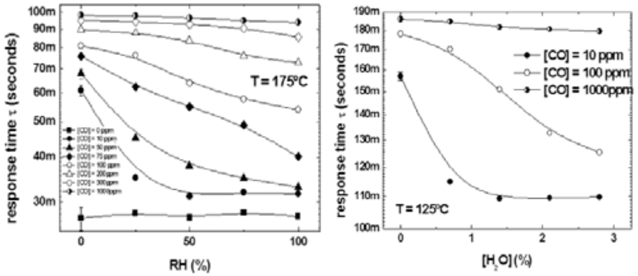
Molecular and monoatomic oxygen



CO response time constants normalized to that of 1000 ppm of CO for different temperatures and CO concentrations ranging from 10 to 1000 ppm. The preference for monoatomic oxygen in competition with molecular oxygen is corroborated before thermal inertia saturates the response time.

CO and humidity

Besides the competition between these two types of oxygen, a more intense competition scenario takes place among different surface sites and competitive gas species. One of the most typical cases corresponds to that of the presence of humidity in the ambient. Consequently, sites with absorbed oxygen compete with sites with hydroxyls. Thus, two different surface reactions with different probabilities can be expected for the impinging CO molecule which can react with the absorbed oxygen or, alternatively, interact with the site containing the hydroxyl group. Obviously, the overall number of transitions with each of the sites depends on both the concentration and probability parameters. Therefore, if the concentration of CO molecules impinging on the surface is small enough, they can react mainly using the faster pathway, i.e. through sites occupied with monoatomic oxygen. In contrast, if a large concentration of CO molecules is impinging on the surface, both types of surface reaction will take place and the slow one can have the larger part of the reactions, appearing as the dominant process occurring at the surface.



CO response time constant for different concentrations of humidity from 0% to 100% measured at 175 and 125 ºC and CO concentrations from 10 to 1000 ppm. Observe that the same levels of humidity are given on two different scales: percentage of relative humidity and global percentage (ppm=10:000).

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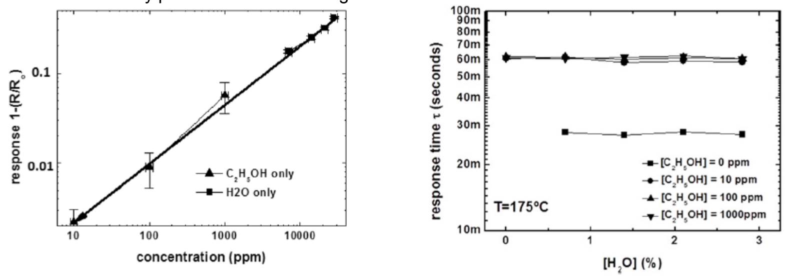
Ethanol and humidity

A completely different scenario is found for other types of molecules which show more complex chemical reaction routes. Two interesting examples are given by ethanol and ammonia molecules. The first of these, in this range of measurement temperatures, decomposes giving as the reacting product a hydroxyl group, which is the same as that introduced by the presence of humidity. Nevertheless, it should be observed that its concentration is much lower. Ethanol molecules, in our working conditions, start their breaking processes of dehydration on acidic sites.The electrical transduction is given by the resulting water molecules after breaking the ethanol ones, giving a similar and linear response to that expected for humidityThe usual ethanol concentration is in the range of 1000 ppm, whereas a low value of relative humidity at room temperature, i.e. 25%, corresponds to approximately 7.000 ppm, and a high value, i.e. 100%, is about 28.000 ppm. It is remarkable to observe the similar sensitivities for ethanol and humidity plotted in the same diagram



Plot of the logarithm of the sensor response versus the logarithm of the ethanol and humidity concentration taken on the same scale.

Response time constants for different concentrations of ethanol and humidity at 175 ºC.

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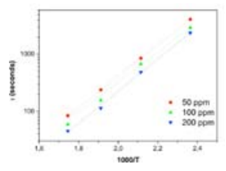
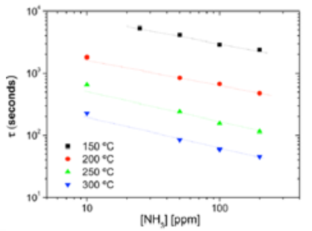
Ammonia and humidity

A completely different scenario is expected for the interaction with ammonia molecules. The reactions of NH3 molecules with metal oxide surfaces are much more complex as they need, unlike the case of ethanol, several decomposition steps starting on a basic site.

The interaction of ammonia with SnO2 have been reported [a]. In this case, under working conditions, non-lattice oxygen (O5c) adsorbed on SnO2 exhibits a more basic character than lattice bridging oxygen (O2c), and consequently, it plays a more significant role in the dehydrogenation of NH3 on SnO2, giving N2 and H2O as the main resulting products. However, this sensing process of ammonia on tin oxide nanowires involves a concomitant chemical nature that is performing ammonia transduction very differently from the previous case. Ammonia requires two molecules for the reaction to take place . It has been experimentally and theoretically shown that the reaction chain taking place involves the interaction between two ammonia molecules and, then, the chemical to electrical transduction only occurs at the end of this multiprocess. In this way, the reaction chain can give as subproducts N2 and a water molecule. These characteristics give rise to a dependence of the response time constant on the ammonia concentration such as has recently been reported [a]. Aside from the energy activation with the temperature, the response time constants are found to depend on $[NH3]^{-1/2}$ which agrees with a molecular meeting probability directly linked to the density of molecules on a surface.





Response time τ to different NH3 concentrations as a function of the working temperature. Experimental data follow an Arrhenius law with an activation energy of Ea = 0.5 eV.

Response time τ dependence on the ammonia concentration. Experimental data fit well to τ ≈ [NH3]−1/2.

[a]Shao F, Hoffmann M, Prades J D, Morante J R, Lopez N and Hernandez-Ramırez F 2013 J. Phys. Chem. C 117 3520

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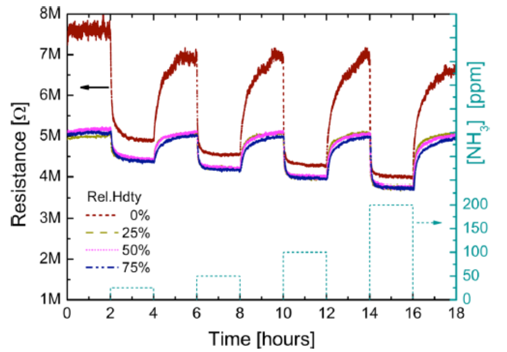
Ammonia and humidity

Under these conditions, in the presence of a certain humidity level (normal humidity concentrations range from 25% to 100% relative humidity, RH, at room temperature), the sensor response saturates, corroborating the high affinity of water for the SnO2 surface and confirming its high coverage by water moieties.



SnO2 nanowire response toward sequential pulses of NH3 (25−200 ppm) in dry air and different humidity levels at a temperature of 250 °C.

[a]Shao F, Hoffmann M, Prades J D, Morante J R, Lopez N and Hernandez-Ramırez F 2013 J. Phys. Chem. C 117 3520

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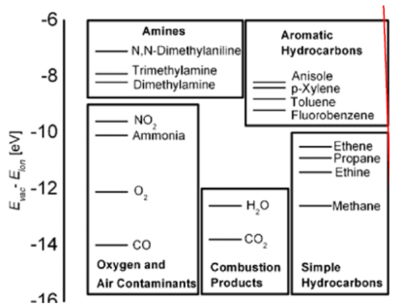
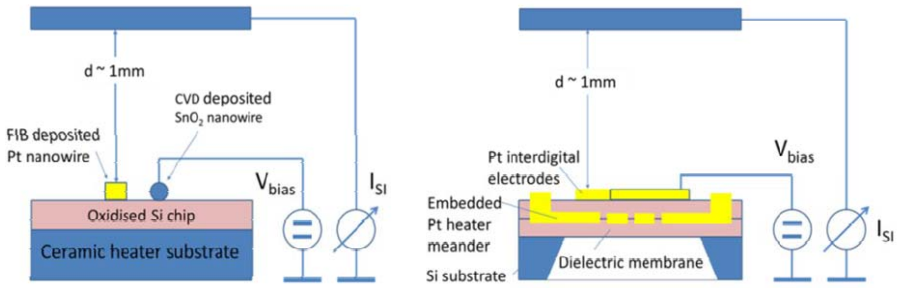
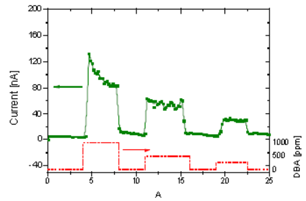
Surface ionization

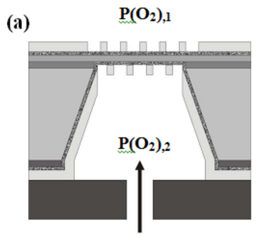


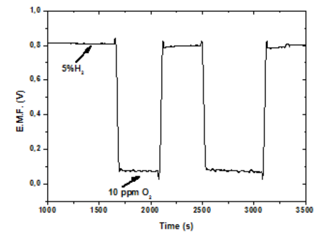
Surface ionization nanosensors

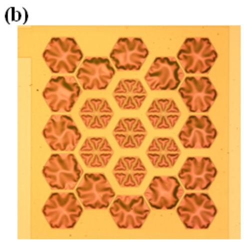


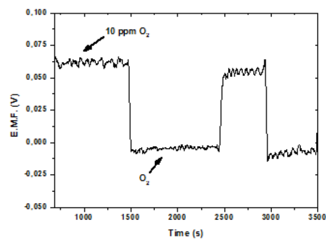


FULLY INTEGRATED LAMBDA SENSOR BASED ON MICROMACHINED PLATFORMS AND YTRIA STABILIZED ZIRCONIA THIN MEMBRANES FOR OXYGEN MEASUREMENT

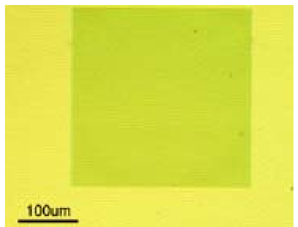


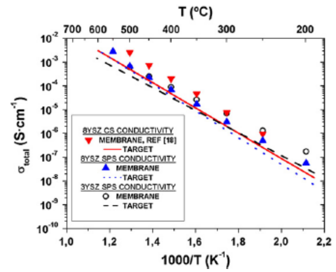






FULLY INTEGRATED ELECTROCHEMICAL SENSOR BASED ON MICROMACHINED PLATFORMS AND YTRIA STABILIZED ZIRCONIA THIN MEMBRANES FOR GAS MEASUREMENT





Garbayo a, G. Dezanneau , C. Bogicevic , J. Santiso , I. Gràcia , N. Sabaté , A. Tarancón,
Solid State Ionics (2012) 216, pp 64-68

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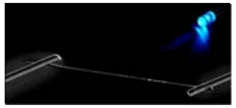
Illumination effects on individual nanowires

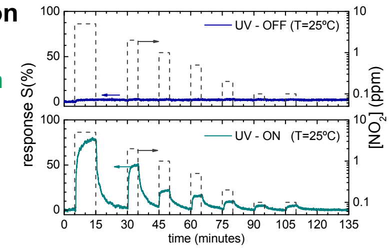
Gas - Light - NW interaction
Room temperature gas sensors phenomenology

Gas response at RT under illumination

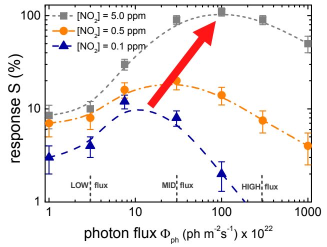
✓ **Better response to NO_2 under illumination**

- Faster recovery (*NO_2 desorption?*)
- …but also higher response! (*competitive behavior?*)





- Maximum response depends on…
  … photon's density
  … NO_2 concentration
  (*$[NO_2]$ - Φ_{ph} balance*)



PHYS. CHEM. CHEM. PHYS., (2009) DOI: 10.1039/b915646a

Gas - Light - NW interaction
RT gas sensors: quantitative model

On the basis of the previous conclusions…

1. Surface consists on a stable set Λ of adsorption sites (O_{Vac}) in a regular arrangement
   Sens.Actuators B. **126** 62 (2007)
   Sens.Actuators B. **126** 6 (2007)
   Thin Sol. Films **515**, 8670 (2007)
2. NO_2 and O_2 molecules compete for the same adsorption sites (O_{Vac})
   J. Electrochem. Soc. **154**, H675 (2007)
   Thin Sol. Films submitted (2008)
   Appl. Phys. Lett. **93**, 123110 (2008)
3. UV photons desorb NO_2 and O_2 molecules from O_{Vac}
   Nanotechnol. **19**, 465501 (2008)
   J. Phys. Chem.C **112**, 19540 (2008)
4. Langmuir approximations
5. Balance rate equations of two populations adsorbed onto the nanowire surface

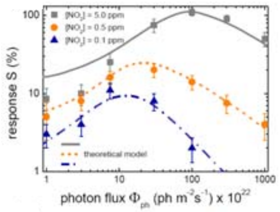
$$\Lambda = n_{OV} + n_O + n_{NO_2}$$

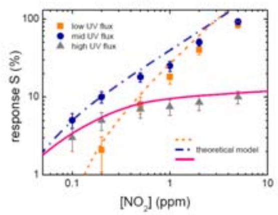
$$\frac{dn_{NO_2}}{dt} = c_{NO_2}(T)\cdot n_{OV}\cdot[NO_2] - \sigma_{NO_2}\Phi_{ph}\cdot n_{NO_2}$$

$$\frac{dn_O}{dt} = c_O(T)\cdot n_{OV}\cdot[O_2] - \sigma_O\Phi_{ph}\cdot n_O$$

chemisorption (at RT) | photodesorption (only)

$$S([NO_2],\Phi_{ph}) = \frac{\left[r_{nw} - \alpha\sqrt{\Delta q_O \cdot \frac{\Lambda\sigma_{NO_2}[O_2]_{SA}c_O}{\sigma_O[NO_2]c_{NO_2} + \sigma_{NO_2}([O_2]_{SA}c_O + \Phi_{ph}\sigma_O)}}\right]^2}{\left[r_{nw} - \alpha\sqrt{\Delta q_O \cdot \frac{\Lambda\sigma_{NO_2}[O_2]_{SA}c_O}{\sigma_O[NO_2]c_{NO_2} + \sigma_{NO_2}([O_2]_{SA}c_O + \Phi_{ph}\sigma_O)}}\sqrt{1 + \frac{\Delta q_{NO_2}}{\Delta q_O}\frac{c_{NO_2}\sigma_O}{\sigma_{NO_2}c_O}\frac{[NO_2]}{[O_2]_{SA}}}\right]^2} - 1$$

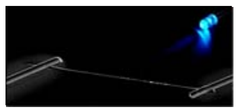




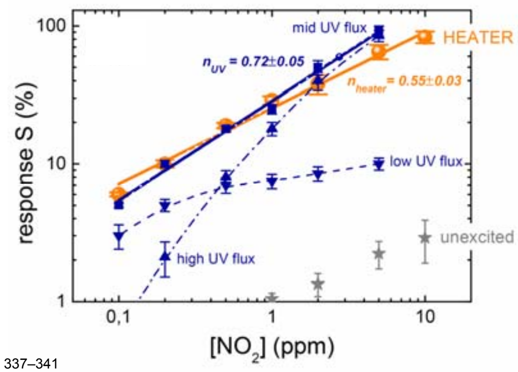
Gas - Light - NW interaction
RT gas sensors: model-based optimization

✓**According to the previous model…**

…photon's density tunes the response.

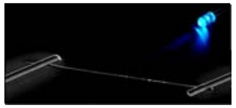


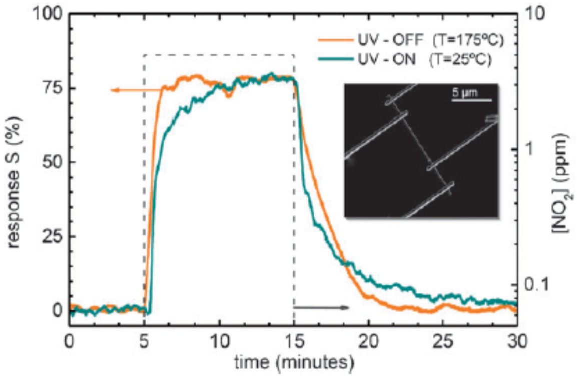
"at the optimum photon's density, the response is comparable to that of conventional (heated) devices"



SENSORS AND. ACTUATORS B: CHEM., 140 (2009) 337–341

Gas – Light – NW interaction
RT gas sensors: model-based optimization





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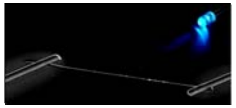
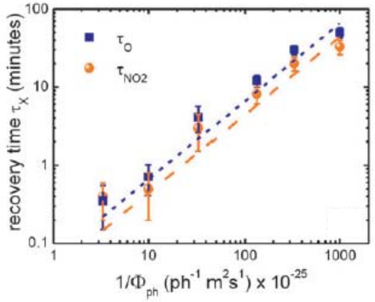
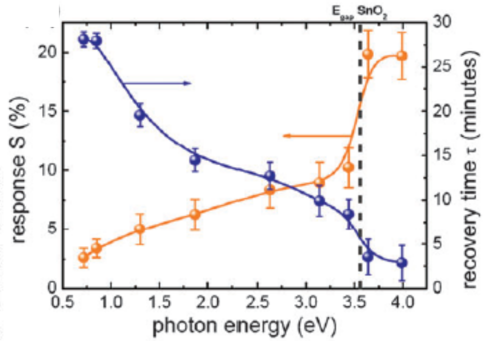
Gas – Light – NW interaction
RT gas sensors: model-based optimization







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Improving selectivity controlling surface nanowire processes

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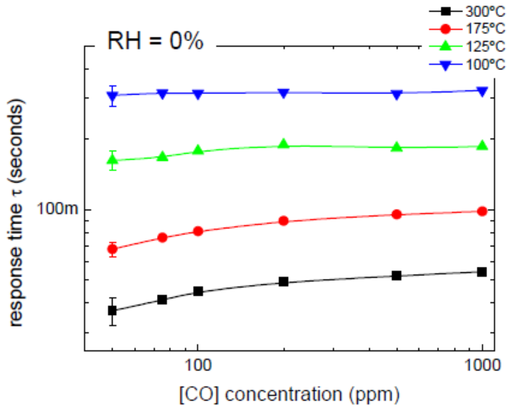
Other possible applications of this experimental procedure



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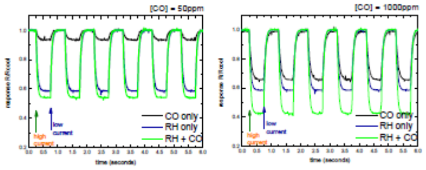
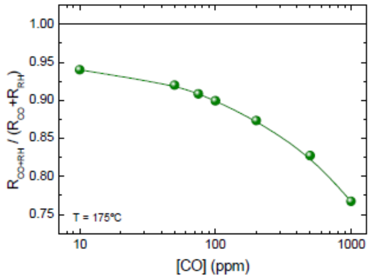
Other possible applications of this experimental procedure





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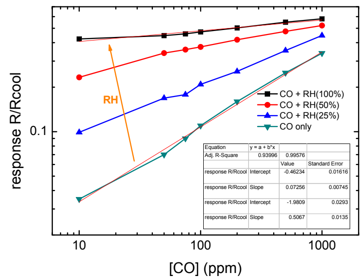

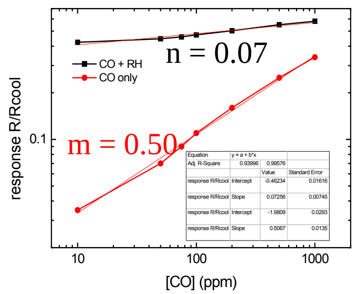

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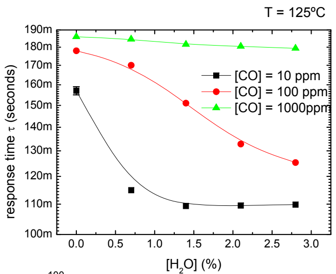

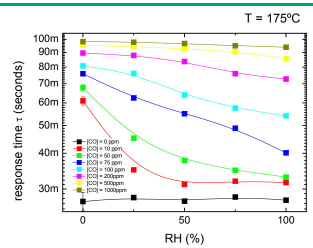

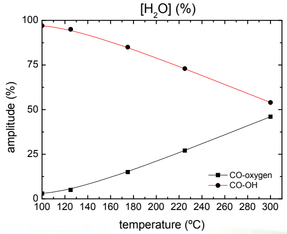

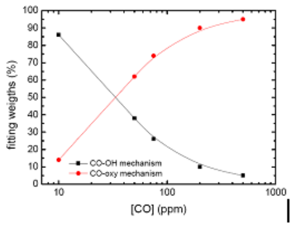

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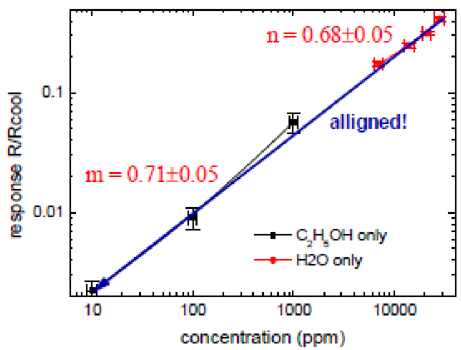

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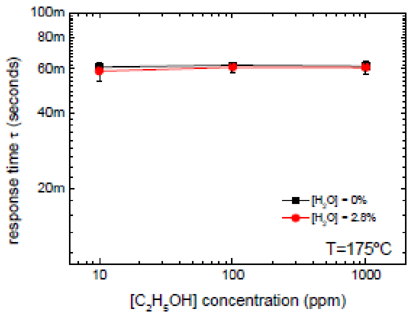

Conclusion

Conductometric gas sensors based on individual nanowires with ultra low power requirements necessary to be operated (only a few tens of microwatts) can be obtained if they make use of the self-heating effect produced by bias current.

These devices exhibit faster dynamic responses in pulsed operation mode than their thin-film counterparts (and thick films), since interfering diffusion processes are eliminated due to their geometry, and pave the way towards more efficient metal oxide gas sensors

Furthermore, these nanowire platforms become a powerful experimental set-up to carried out fundamental basic study on the chemical electrical transduction mechanisms.

The performances of individual nanowire platforms point out their potential as gas sensors. The main challenge nowadays is how the individual nanowire manipulation and associated processes could be moved from the laboratory to commercial scale.

Conclusion

Tools for studying chemical electrical transduction mechanisms, avoiding hidden and masked information originating from polycrystalline grain boundaries are needed. Moreover, due to the self-heating capability for control of the nanowire temperature as well as their low thermal inertia, these platforms, unlike more standard thin/thick film gas sensors, facilitate temperature pulsed working modes giving rise to the achievement of worthy response time constant information as reliable signatures of the surface chemical reactions.

According to this methodological approach detailed results on the influence of humidity on three different types of molecules have been presented, pointing out different kinds of behavior:

CO molecules have been found to compete between the absorbed oxygens and absorbed hydroxyls. The influences of the concentration and of the temperature have been determined. The differences between low and high concentrations confirm the competitive character among the two sites which converts the sensing procedure in non-lineal.

Ethanol molecules, in our working conditions, start their breaking processes of dehydration on acidic sites.The electrical transduction is given by the resulting water molecules after breaking the ethanol ones, giving a similar and linear response to that expected for humidity.

Ammonia molecules have been found, in our working conditions, to follow a dehydrogenation process on basic sites.Moreover, a meeting between two ammonia molecules at the same site is needed to achieve the complete reaction chain. A high concentration of water molecules, in the range of a few thousands to approximately 28.000 ppm (15–100%of RH at room temperature), caused by the presence of humidity, gives huge difficulties in facilitating a meeting of two ammonia molecules, in the concentration range of ppm and, consequently, the ammonia sensor response is almost canceled.

Conclusion

The selected species (CO, H2O, ethanol and NH3) give a clear example of the outstanding role played by the competitiveness and their different consequences on the selectivity of gas sensors. Likewise, the data obtained and procedure used can help to improve sensor design, enhancing selectivity or avoiding negative crossing effects due to interfering gases like humidity.

New processes based on surface ionization (SI) on nanostructured materials have also been reported as relevant alternatives. These new SI nanodevices appear as a promising pathway for improving selectivity on the basis of the differences that exist among the ionization energies corresponding to the target species and the high ionization efficiency shown by nanowires.

Likewise, NEW flashing and exciting alternatives are revealed for the new fully integrated all solid state electrochemical gas sensors, that NOWADAYS constitutes the bigger market of GAS SENSORS.

Acknowledgement

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