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

COST Action TD1105

1ST TRAINING SCHOOL

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GAS SENSORS: PRINCIPLES OF OPERATION AND SENSOR PARAMETERS

ENEA
AGENZIA NAZIONALE PER LE NUOVE TECNOLOGIE, L'ENERGIA E LO SVILUPPO ECONOMICO SOSTENIBILE

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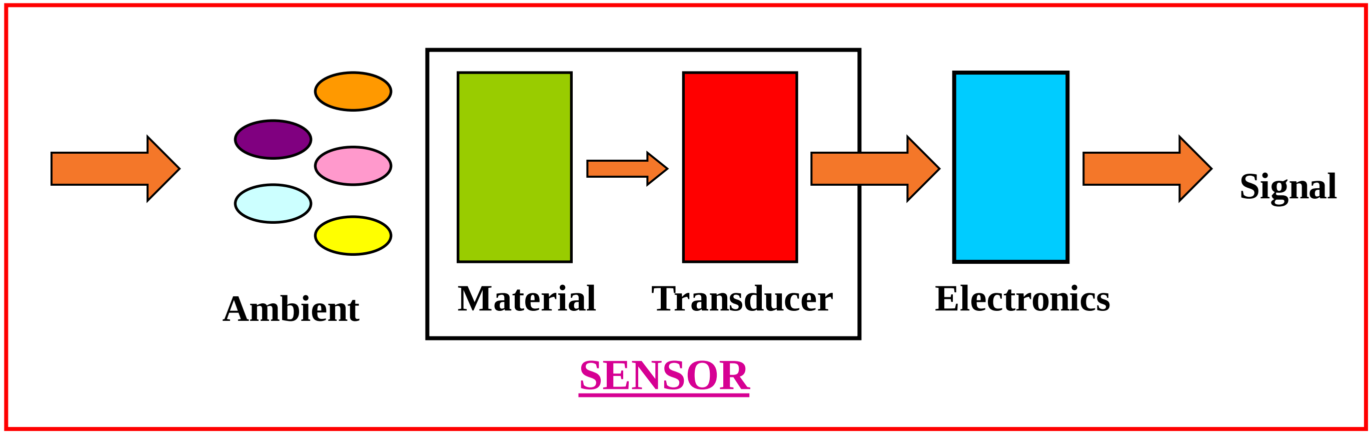
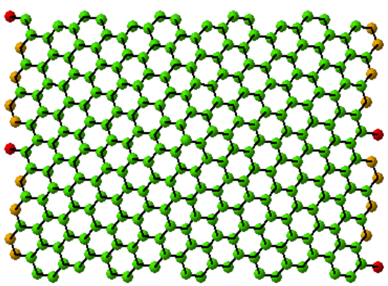
OUTLINE

- Description of Sensors and Transducers
- Classification of Gas Sensors
- Principles of Operations for Gas Sensors
- Sensor Parameters for Solid-State Sensors
- Examples of Chemical Sensors
- Current Aspects on Air Quality Sensors
- Concluding Remarks

WHAT IS A HIGH-PERFORMANCE GAS SENSOR ?





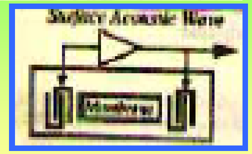
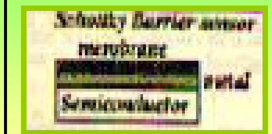
SWCNTs

SENSOR MATERIALS:

- ✓ Metal Oxides Thin-Films: SnO_2, WO_3, ZnO, etc
- ✓ Conduct. Polymers: Polypyrrole, Polythiophene, etc.
- ✓ Carbon Nanotubes
- ✓ Graphene
- ✓ Organic Materials
- ✓ Hybrid Materials

- ✓ HIGH SENSITIVITY
- ✓ FAST RESPONSE
- ✓ FAST RECOVERY
- ✓ REVERSIBILITY
- ✓ STABILITY
- ✓ REPEATABILITY
- ✓ LOW NOISE AND HIGH RESOLUTION
- ✓ LOW DETECTION LIMIT

Materials and Transducers for Gas Sensors

	TRANSDUCERS					
	$\Delta c \Rightarrow \Delta\sigma \Rightarrow \Delta i \Rightarrow \Delta v$ 	$\Delta c \Rightarrow \Delta M \Rightarrow \Delta f$ 	$\Delta c \Rightarrow \Delta M \Rightarrow \Delta f$ 	$\Delta c \Rightarrow \Delta\sigma \Rightarrow \Delta i \Rightarrow \Delta v$ 	$\Delta c \Rightarrow \Delta n \Rightarrow \Delta I \Rightarrow \Delta i \Rightarrow \Delta v$ 	$\Delta\Phi \Rightarrow \Delta i \Rightarrow \Delta v$ 
SENSOR MATERIALS	MOSFET	QCM MEMS	SAW TFBAR	CHEMI-RESISTOR	OPTICAL	SCHOTTKY
METAL-OXIDE FILMS (SnO_2, ZnO, WO_3, ..)						
CONDUCTING POLYMERS						
THICK FILMS						
RECEPTORS						
ENZYMES						
ANTIBODIES						
ORGANIC FILMS						
DNA						
NANOMATERIALS				CNTs		

Selected Principles of Operation for Gas Sensors

Transducer	Principle of operation	Measurand Input / Signal Output
Conductometric	*Electrical Conductivity*: Conducting Polymers; Metal Oxides	$\Delta c \rightarrow \Delta\sigma \rightarrow \Delta i \rightarrow \Delta V$
Optical	Absorption; Emission; Fluorescence; Chemiluminescence; Evanescent Wave; Fiber Optics	$\Delta c \rightarrow \Delta n \rightarrow \Delta I \rightarrow \Delta i \rightarrow \Delta V$
Electrochemical	*Ionic Conductivity*: Amperometric; Potentiometric; Voltammetric	$\Delta c \rightarrow \Delta\sigma \rightarrow \Delta i \rightarrow \Delta V$
Thermal	*Flow of thermal energy*: Catalytic; Pyroelectric; Calorimetric	$\Delta c \rightarrow \Delta T \rightarrow \Delta i \rightarrow \Delta V$
MOSFET	Charge capacitive coupling	$\Delta c \rightarrow \Delta\Phi \rightarrow \Delta i \rightarrow \Delta V$
Ultrasonic (Mechanical or Acoustic)	*Piezoelectricity*: QCM; SAW; TFBAR	$\Delta c \rightarrow \Delta m \rightarrow \Delta f$ $\Delta c \rightarrow \Delta m \rightarrow \Delta f, \Delta\varphi$

Δc = variation of concentration; $\Delta\sigma$ = variation of electrical conductivity; Δi = variation of current; ΔV = variation of voltage; Δn = variation of refractive index; ΔI = variation of light intensity; ΔT = variation of temperature; $\Delta\Phi$ = variation of work function; Δm = variation of mass; Δf = variation of frequency; $\Delta\varphi$ = variation of phase of acoustic wave

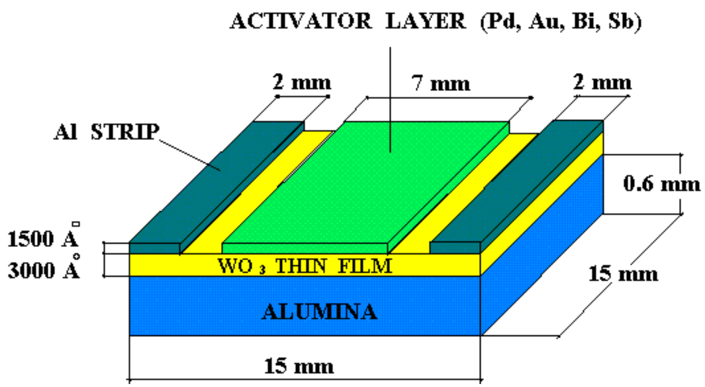
GAS SENSORS CLASSIFIED by TRANSDUCERS

Transducer	Principle of operation
Chemoresistor	***Electrical Charge Transfer***
Electrochemical	***Ionic Conductivity*****:** **Amperometric; Potentiometric; Voltammetric**
Capacitors	***Dielectric Constant***
Field Effect Transistor	***Electrical Charge Channel***
Piezoelectric	***Mass Loading (Viscoelastic and Acoustoelectric Loading)*****:** **QCM; SAW; TFBAR**
MEMS	***Mass Loading*****:** **Micro-Electrical-Mechanical-Systems**
Thermal	***Flow of thermal energy*****:** **Catalytic; Pyroelectric; Calorimetric**
Optical	***Refractive Index***

Type of Sensor: CHEMIRESISTOR (1/6)

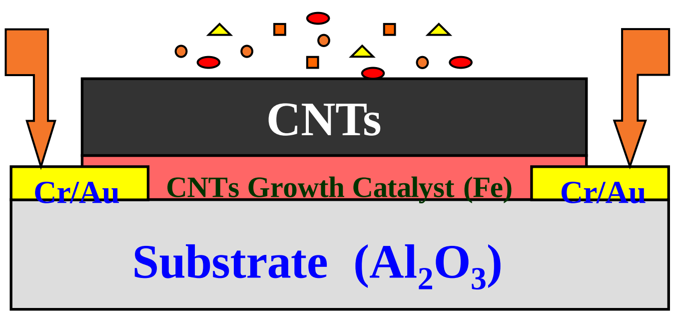
Two-Pole Conductometric Thin-Film Gas Sensors

Metal-doped Metal Oxide (MOX) Gas Sensor



A transfer of **electrical charge** (carrier) occuring between targeted gases (**electro-donating** or **electro-accepting**) with sensitive semiconductor materials of ***n-type*** **(MOX)** or ***p-type*** **(CNT)**.

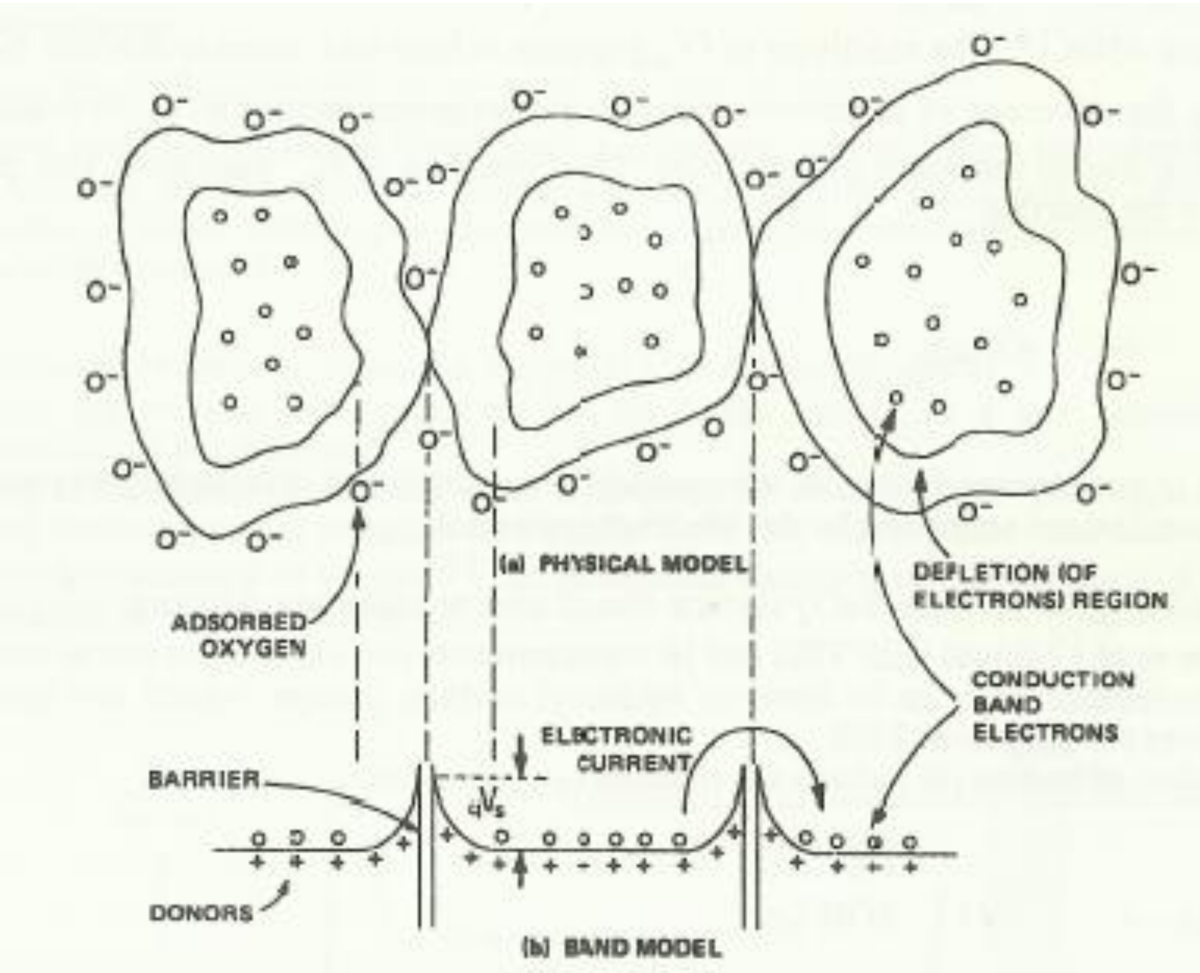
Carbon Nanotube (CNT) Gas Sensor



Class of Sensor Materials	n-type	p-type
Metal Oxides (MOX) (SnO_2, ZnO, WO_3, TiO_2, ZrO_2, Al_2O_3, etc.)	X	
Carbon Nanotubes (CNTs)		X
Conducting Polymers (CP) (Polypyrrole, Polythiophene, Polyacetylene, etc.)		X
Organic Materials	-	-

Type of Sensor: CHEMIRESISTOR (2/6)

Energy bands at the grain boundary for polycrystalline SnO_2



Madou and Morrison equations:

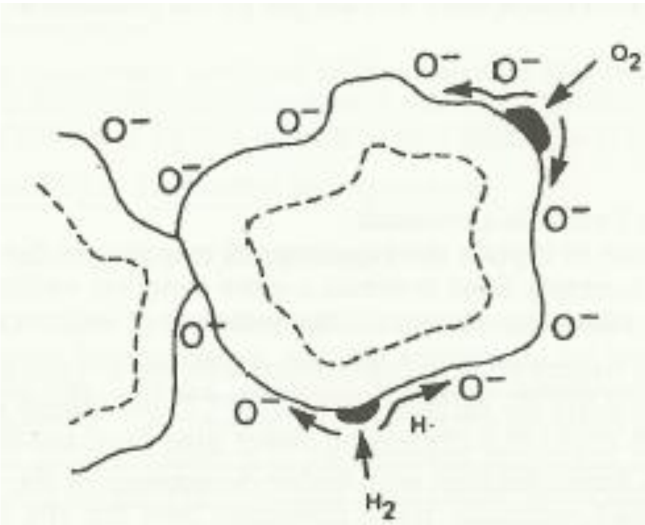
$$CO + O_2^- \rightarrow CO_2 + 2e^-$$
$$CO + O^- \rightarrow CO_2 + e^-$$

$$G = G_0 + k\,(P_{CO})^m$$

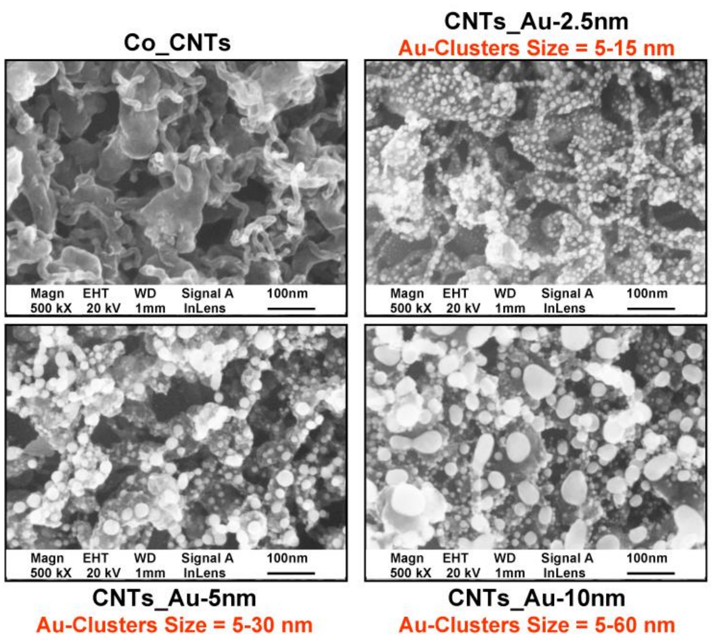
G = Conductance
G_0 = Initial Conductance
k = constant
P_{CO} = CO partial pressure
m ≈ 0.5

Type of Sensor: CHEMIRESISTOR (3/6)

Metal-modifications and catalysts



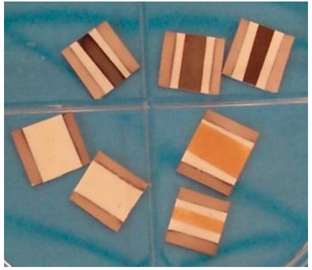
Spillover is the mechanism which is related to the presence of **catalysts** (e.g., *noble metals: **Pt, Pd, Au, Ag**, etc.)* onto the semiconductor surface. Supported catalysts (e.g., Pt) dissociate gas molecules (H_2 or O_2) to be detected; the oxygen and hydrogen atoms *spill over* the semiconducting surface and the reaction rates of the tested gases on the sensor surface are enhanced for improved gas sensitivity and detection limit, at lower sensor operating temperatures (room temperature).



Gold (Au) nanoclusters (size ranging from10 to 50 nm) onto Carbon Nanotube layers for Gas Sensors by ENEA

M. Penza et al., Journal of Sensors, 2008, 107057
M. Penza, et al., Sensors and Actuators B, 140(1) (2009) 176-184

Type of Sensor: CHEMIRESISTOR (4/6)



Gas Sensors by ENEA

Electrical Behaviour of Chemoresistors

Class of Target Gas	n-type Material	p-type Material
Electron-donating Gases (Reducing Gases): CO, NH_3, H_2, H_2S, SO_2, CH_4, CO_2, etc.	Resistance DECREASE	Resistance INCREASE
Electron-accepting Gases (Oxidising Gases): NO_2, O_2, O_3, etc.	Resistance INCREASE	Resistance DECREASE

Electron charge transfer generates conductivity change in the gas sensors:

Reducing gases induce an increase in the electrical resistance of CNTs sensors (p-type)

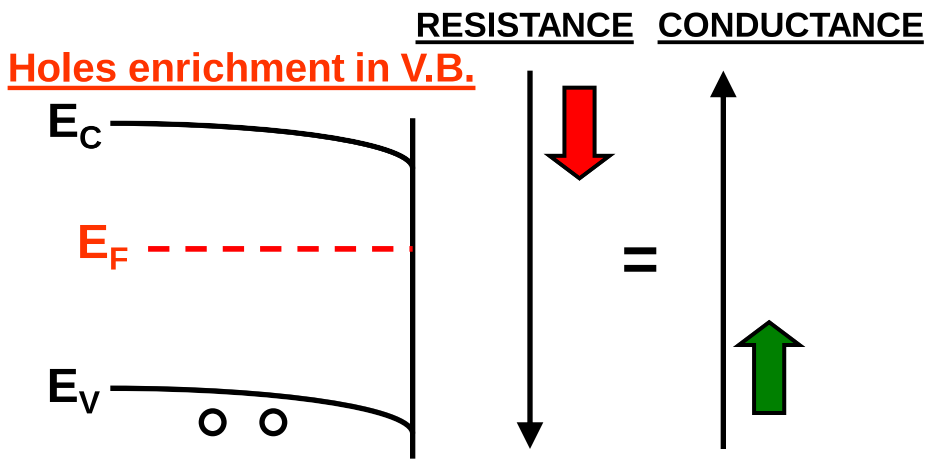
Oxidizing gases induce a decrease in the electrical resistance of CNTs sensors (p-type)

Type of Sensor: CHEMIRESISTOR (5/6)

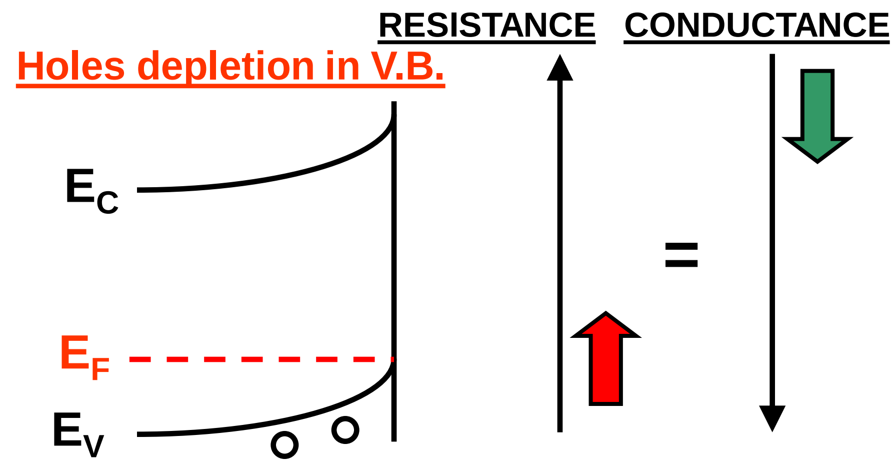
MODEL OF *p-type* CHARGE TRANSFER IN THE SEMICONDUCTING FUNCTIONALIZED CARBON NANOTUBES FILMS GAS SENSORS

UNMODIFIED CNTs: MODEL OF DIRECT INJECTION OF ELECTRICAL CHARGE

Electron-acceptor gases (NO_2, O_2)

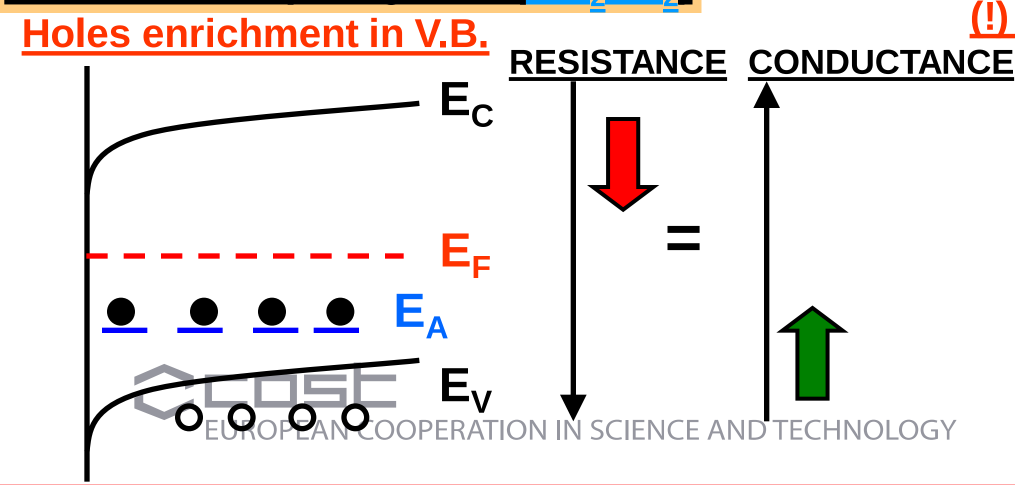


Electron-donating gases (NH_3, H_2S, CO)

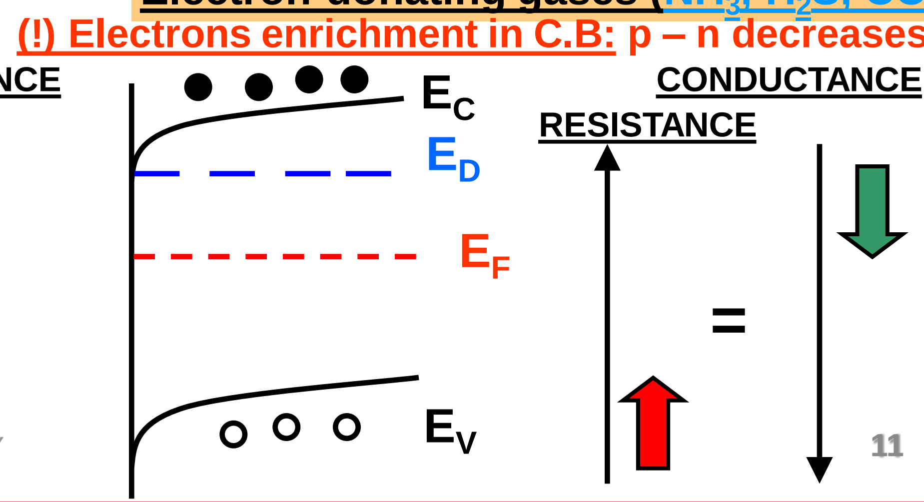


FUNCTIONALIZED CNTs: MODEL OF CATALYTICALY-INDUCED CHARGE TRANSFER

Electron-acceptor gases (NO_2, O_2)

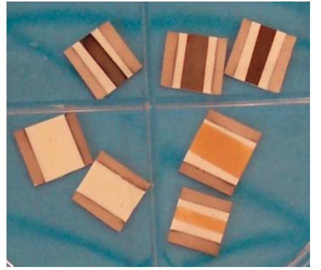


Electron-donating gases (NH_3, H_2S, CO)

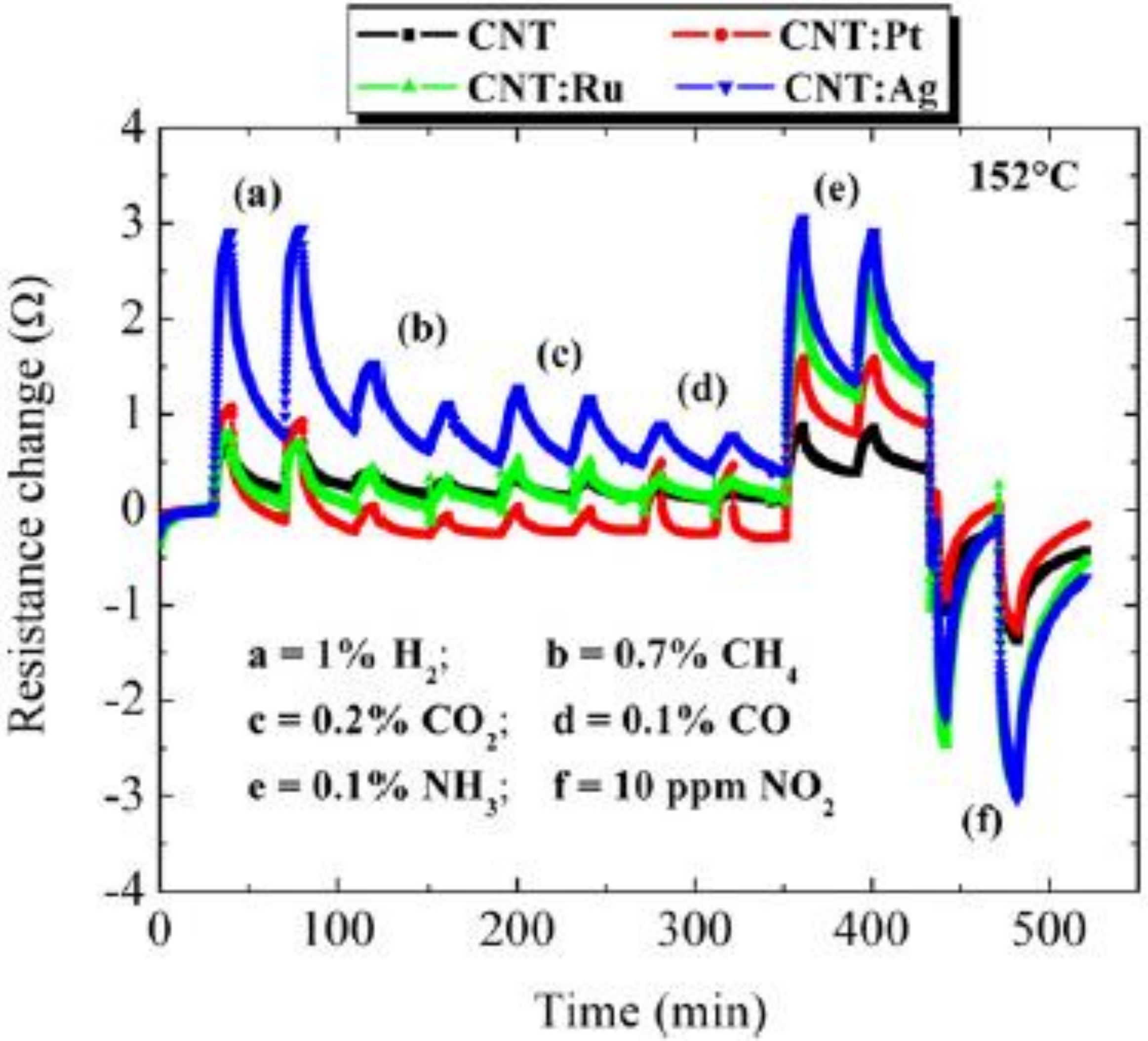


Type of Sensor: CHEMIRESISTOR (6/6)

Some Gas Responses of a Chemoresistor



Gas Sensors by ENEA



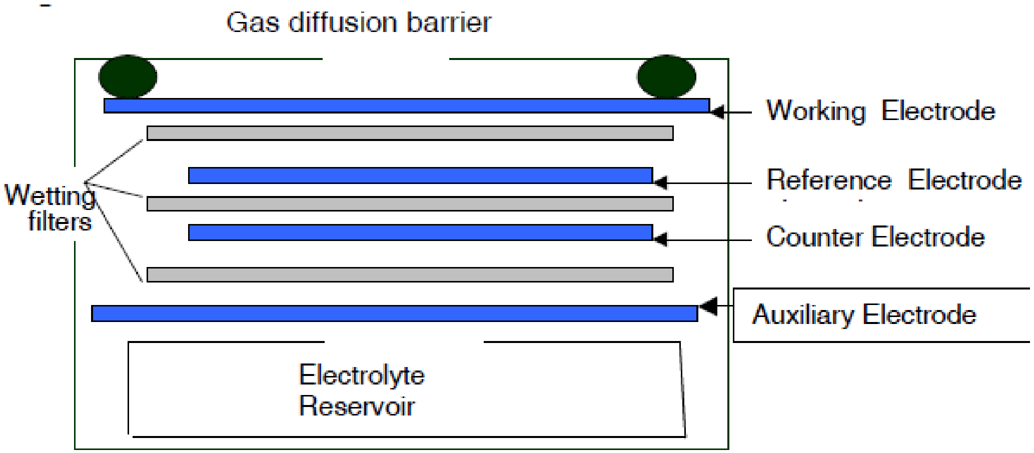
NO_2 oxidizing gas induces a decrease in the electrical resistance of CNTs sensors (p-type)

Reducing gases (CO, NH_3, H_2, CH_4, CO_2) induce an increase in the electrical resistance of CNTs sensors (p-type)

M. Penza et al., Nanotechnology, 21 (2010) 105501

Type of Sensor: ELECTROCHEMICAL

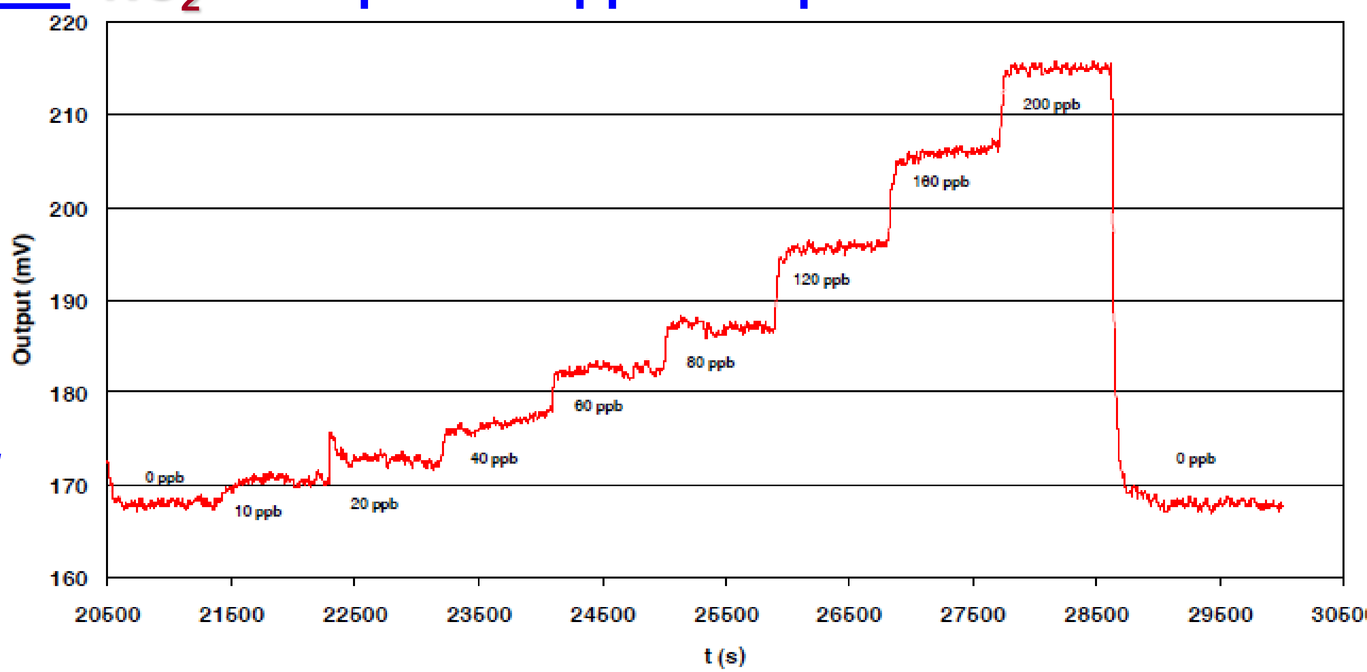
Electrical charge exchange between gas and ionic conductor



Electrochemical gas sensors are cells whose output electrical signal is directly related to the concentration or partial pressure of the gaseous species. Depending on whether the output signal is an electromotive force or a current, the device may be classified in ***potentiometric*** or ***amperometric*** electrochemical sensors.

B4 family sensors: NO_2 test up to 200 ppb in Alphasense Lab

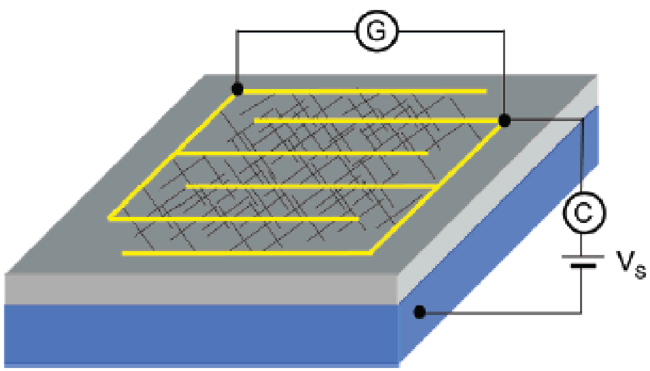
John Saffell, Alphasense Ltd

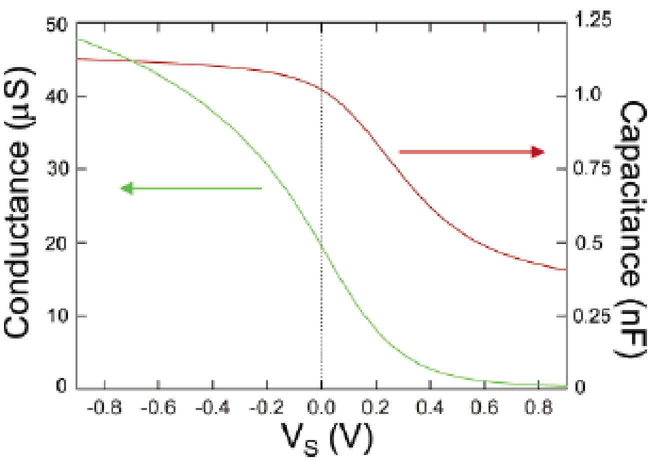


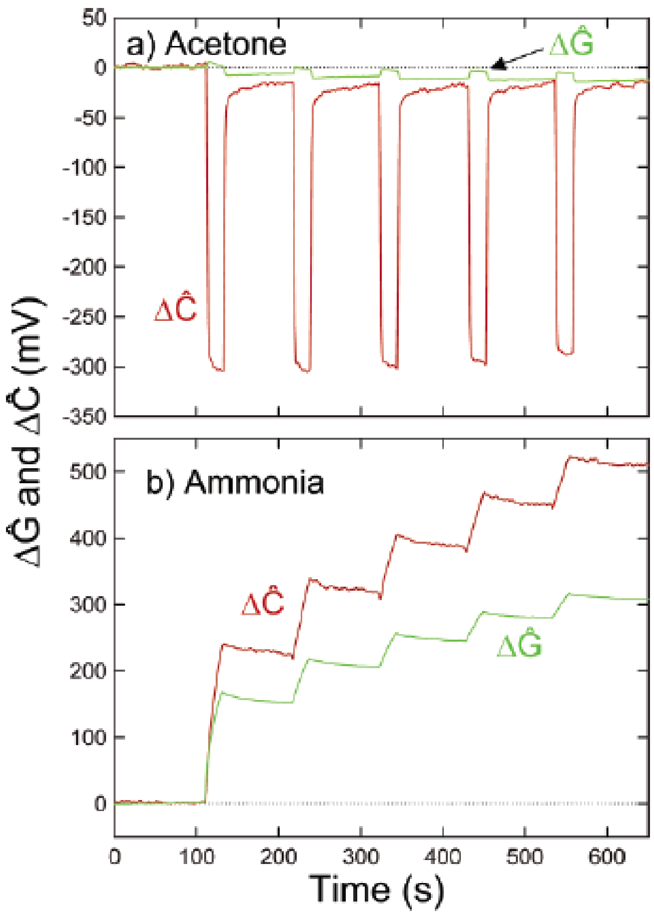
EUROPEAN COOPERATION IN

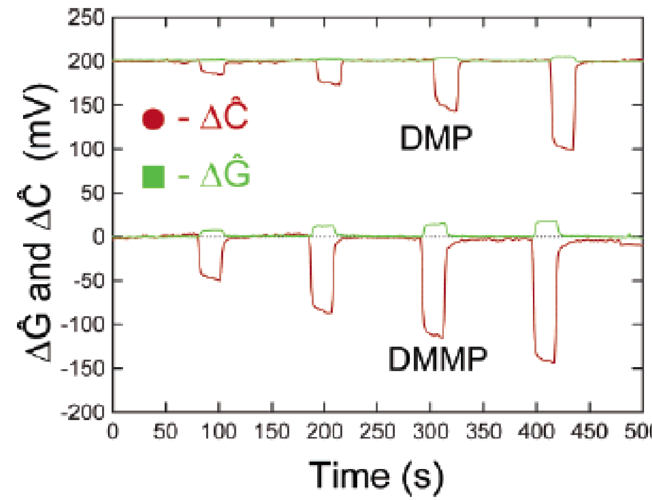
Type of Sensor: CAPACITORS & CHEMIRESISTORS

The capacitance between two parallel electrodes in the Capacitor is modulated by the dielectric constant of a sensing material under gas exposure.









DMP - Dimethyl Phosphite
DMMP - DimethylmethylPhosphonate

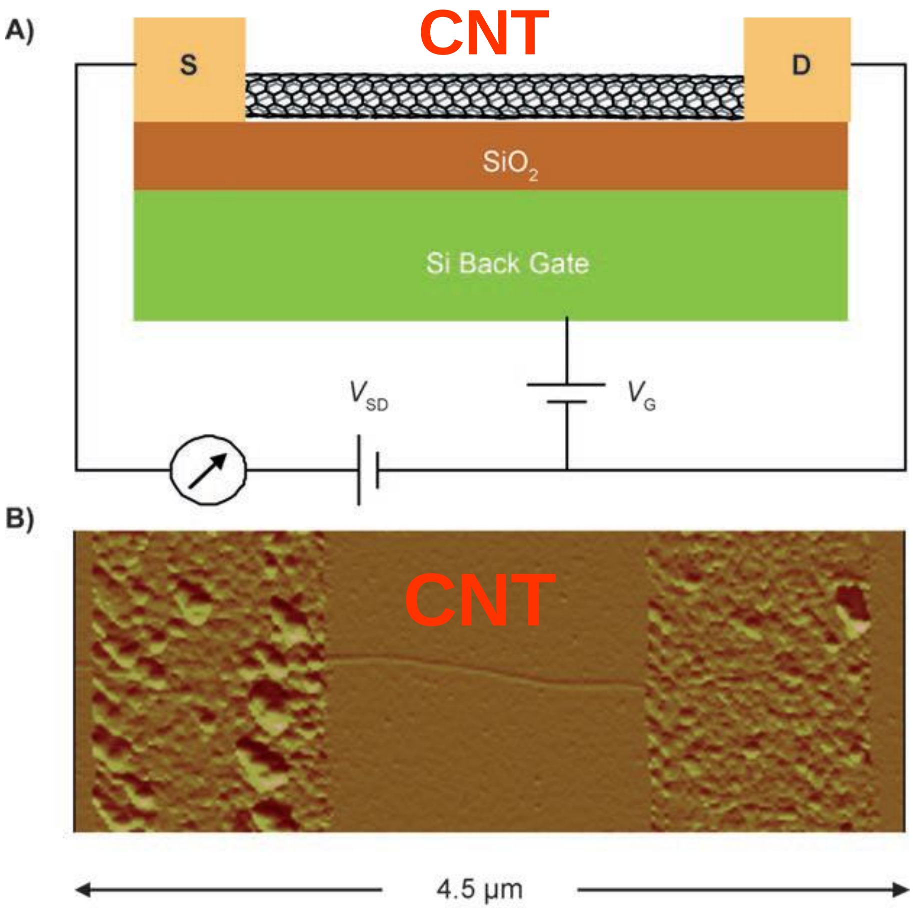
Table 1. Values of $\Delta\hat{G}/\Delta\hat{C}$ Measured for Various Chemical Vapors

chemical vapor	$\Delta\hat{G}/\Delta\hat{C}$
dinitrotoluene	0.20
dichloropentane	0.10
nitrobenzene	0.080
water	0.045
hexane	0.043
toluene	0.025
benzene	0.013
2-propanol	−0.027
acetone	−0.03
tetrahydrofuran	−0.10
DMMP	−0.12

E. S. Snow et al., NANOLETTERS, 5-12 (2005) 2414-2417

Type of Sensor: FIELD EFFECT TRANSISTORS

The current between Source (S) and Drain (D) in the Fielf Effect Transistor (FET) is modulated by the voltage of a back Gate (G) under gas exposure.



D. R. Kauffman et al., Angew. Chem. Int. Ed., 47 (2008) 6550-6570

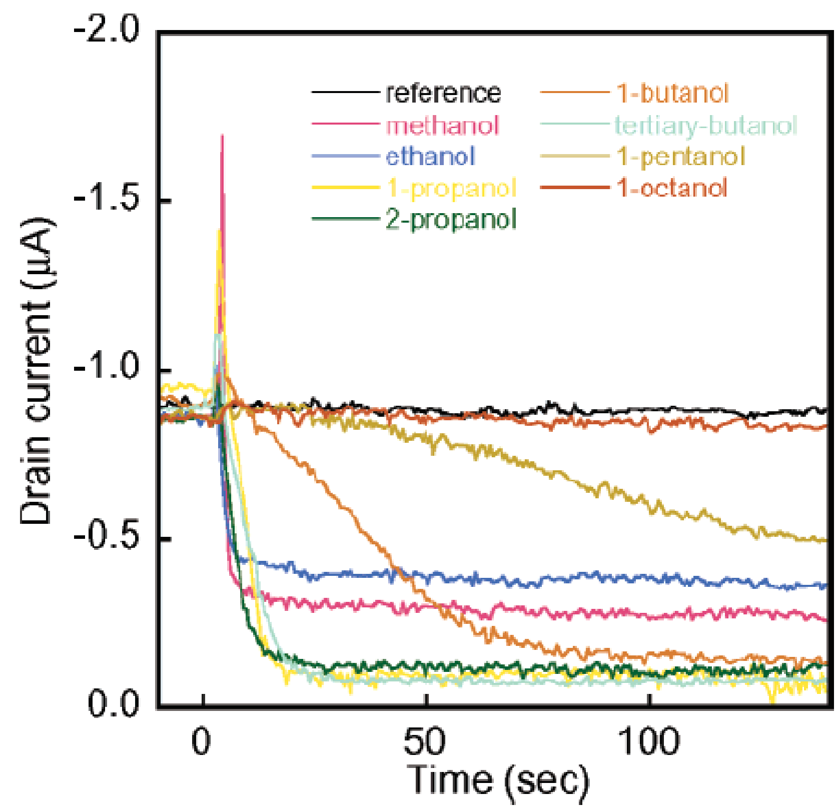
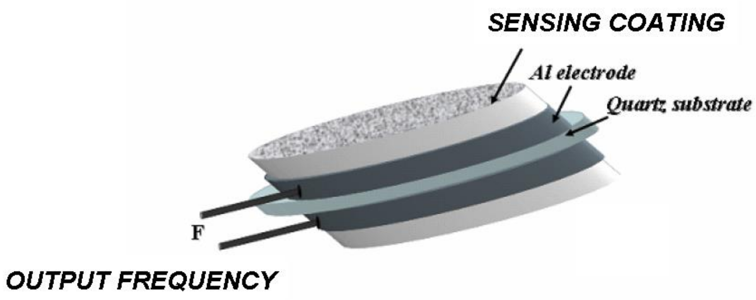


Figure 5. Drain currents for $V_{sd} = -100$ mV and $V_g = -20$ V are shown as a function of time for application of saturated vapor of various kinds of alcohols: methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, tertiary-butanol, 1-pentanol, and 1-octanol.

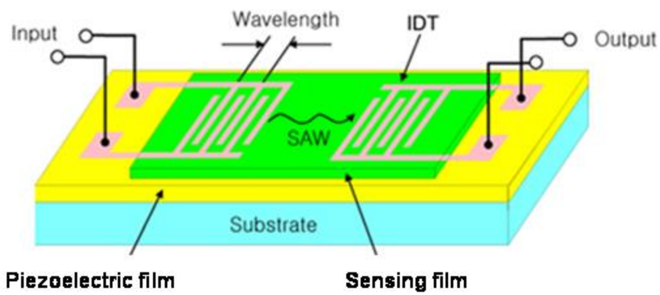
T. Someya et al., NANOLETTERS, 3-7 (2003) 877-881

Type of Sensor: PIEZOELECTRIC (1/6)

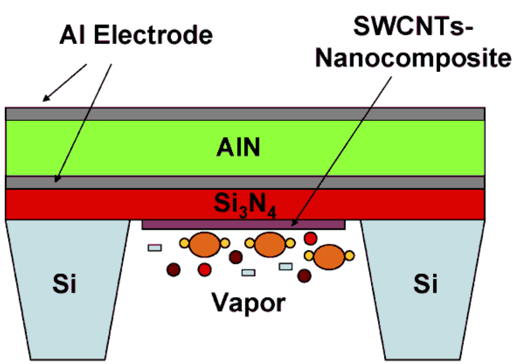
MASS-SENSITIVE ACOUSTIC WAVE DEVICES



- **BAW (Bulk Acoustic Wave) - QCM (Quartz Crystal Microbalance) at a resonating frequency ranging from 5 to 30 MHz.**



- **SAW (Surface Acoustic Wave) at a high resonating frequency ranging from 50 MHz to 1 GHz.**



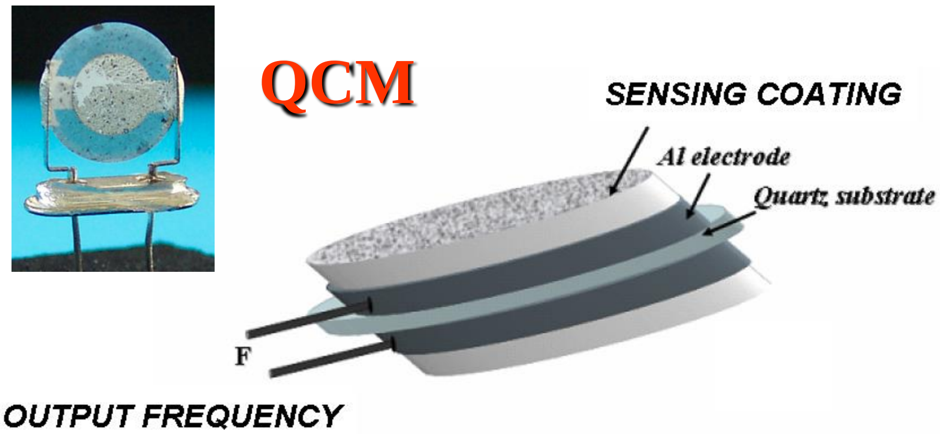
- **TFBAR (Thin Film Bulk Acoustic Resonator) at a resonating frequency ranging from 1 to 10 GHz.**

Type of Sensor: PIEZOELECTRIC (2/6)

QCM - QUARTZ CRYSTAL MICROBALANCE

SENSING MECHANISM: MASS LOADING OF QCM RESONATOR SENSOR

The resonating frequency of a piezoelectric material (e.g., AT-cut quartz), configured as oscillator, is modulated by the adsorbed mass of gas molecules in active material



Sauerbrey equation (1959):

$$\Delta f = S_m f_o^{\,2} \frac{\Delta m}{A}$$

$$S_m = \lim_{\Delta m \to 0} \frac{(\Delta f / f)}{(\Delta m / A)}$$

$S_m =$ *mass sensitivity*

$\Delta m =$ *mass change*

$\Delta f =$ *frequency change*

$f =$ *resonant frequency*

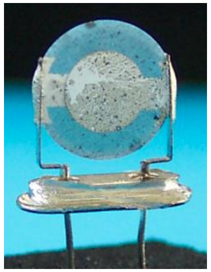
$A =$ sensing *area*

Acoustic device type	Mass sensitivity (cm^2/g)	Frequency range
QCM	10 – 20	5 – 30 MHz
SAW	200 – 400	50 – 1000 MHz

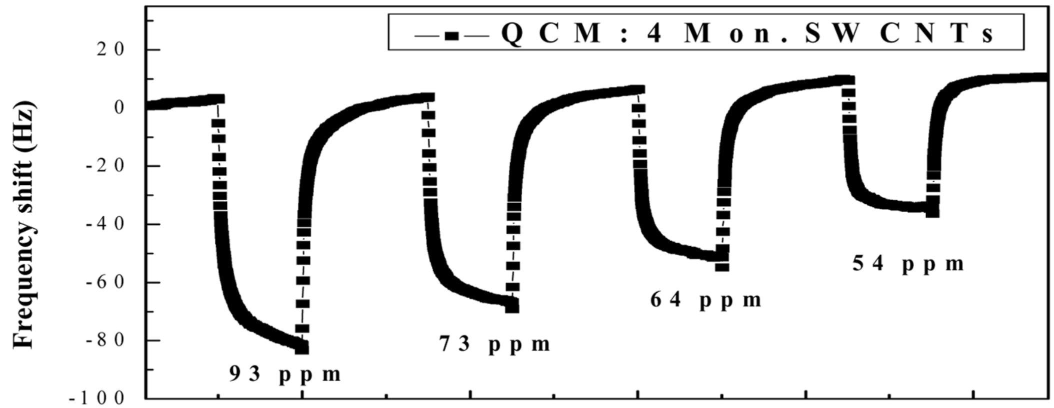
Type of Sensor: PIEZOELECTRIC (3/6)

QCM - QUARTZ CRYSTAL MICROBALANCE

OSCILLATORS FOR QCM RESONATOR SENSORS



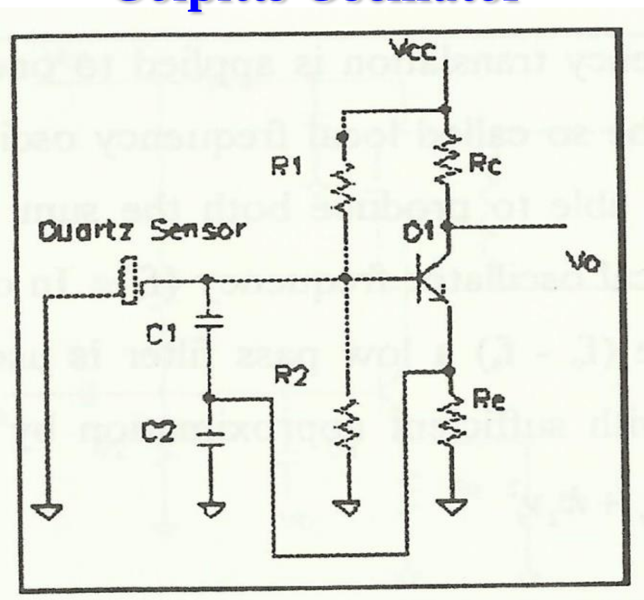
QCM



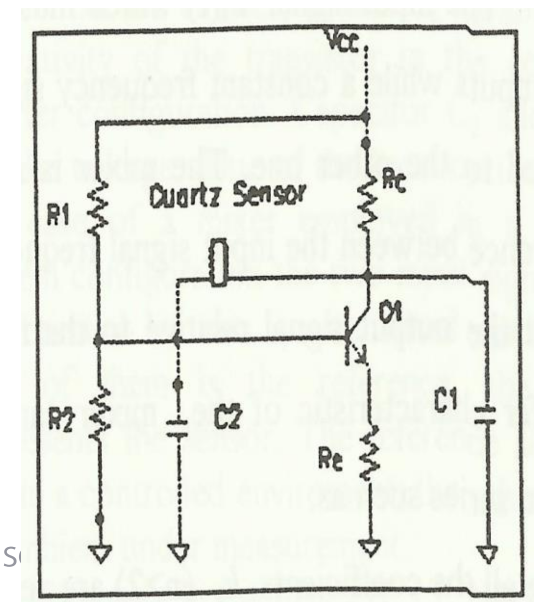
Response of a 10 MHz QCM sensor coated with layer of Single-Walled Carbon Nanotubes exposed towards Xylene vapors, at room temperature

M. Consales et al., IEEE Trans NANO, 6-6 (2007) 601-612

Colpitts Oscillator



Pierce-Miller Oscillator



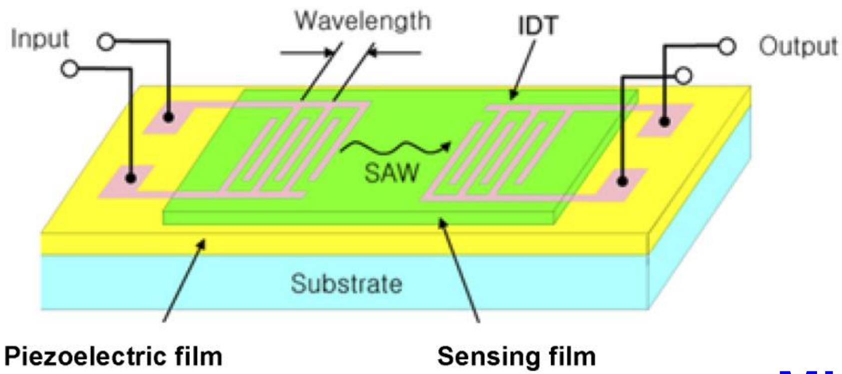
Type of Sensor: PIEZOELECTRIC (4/6)

SAW - SURFACE ACOUSTIC WAVES

SAW

$$\Delta f = -c_m f_o^2 \Delta\rho_s + c_e f_o^2 \Delta\left[hG'\right] - \frac{K_t^2}{2}\Delta\left[\frac{\sigma_s^2}{\sigma_s^2 + v_o^2 C_o^2}\right]$$

(ML) **(VL)** **(AL)**



$$\Delta f_V = \Delta f_M C_V \frac{K}{\rho_S}$$

$$K = \frac{C_S}{C_V}$$

ML = *Mass Loading*

VL = *Viscoelastic Loading*

AL = *Acoustoelectric Loading*

Δf = frequency shift

c_m = mass sensitivity coefficient

f_o = fundamental SAW resonant frequency

Δm = mass change at the surface of membrane

A = area of the SAW sensing membrane

ρ_S = density of the sorbent phase of the analyte

G' = real part of the shear modulus, G

K_t^2 = electromechanical coupling coefficient

v_o = unperturbed velocity of the SAW

σ_S = sheet conductivity of the sensing film

C_0 = capacitance per unit length of SAW substrate

$C_0 = \varepsilon_s + \varepsilon_0$

ε_s = permettivity of substrate

ε_0 = permettivity of free space

K = partition coefficient

C_S = concentration of vapor in the sorbent phase

C_V = concentration of vapor in the vapor phase

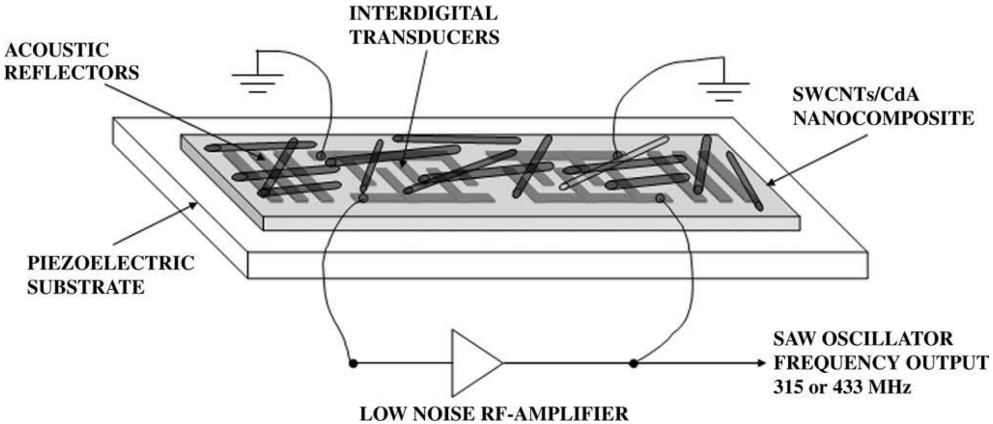
Δf_V = frequency shift due to mass loading

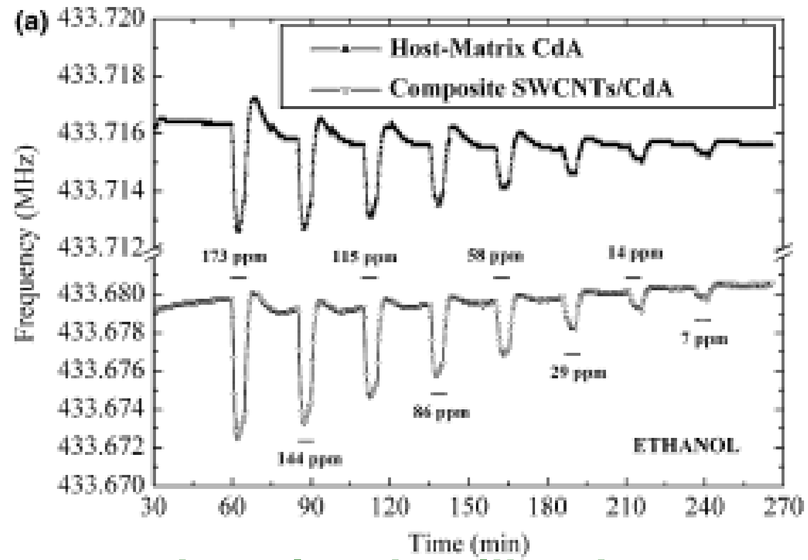
Δf_M = frequency shift caused by sorbent phase

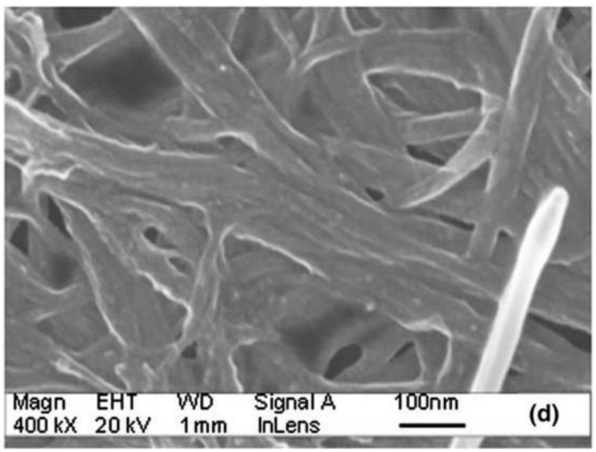
M. Penza et al., IEEE Trans UFFC, 45-5 (1998) 1125-1132

Type of Sensor: PIEZOELECTRIC (5/6)

SAW - SURFACE ACOUSTIC WAVES

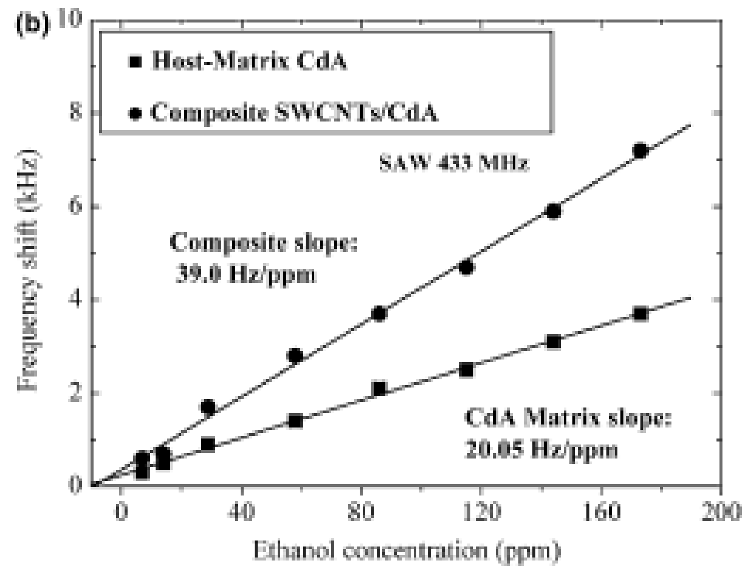






SAW Response to Ethanol and Calibration Curve

CdA = Cadmium Arachidate
SWCNT = Single-Walled Carbon Nanotubes

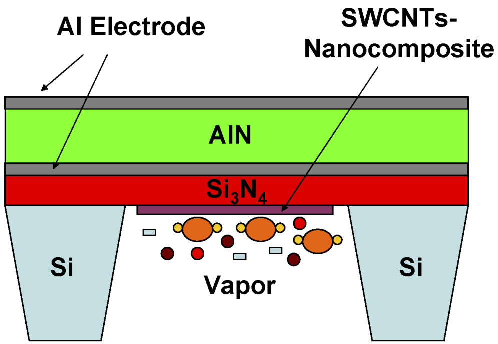


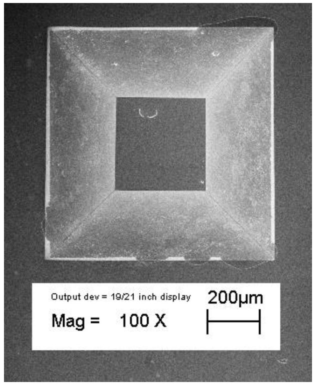
SWCNTs-CdA Nanocomposite

M. Penza et al., Chem. Phys. Lett., 409 (2005) 349-354

Type of Sensor: PIEZOELECTRIC (6/6)

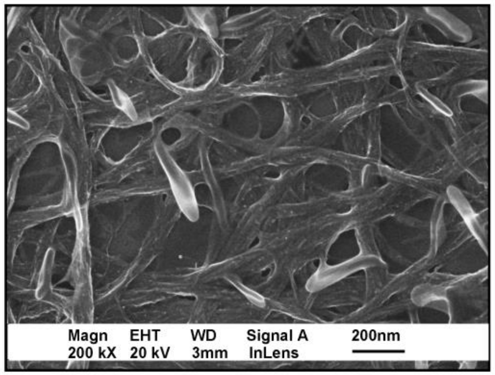
TFBAR - THIN FILM BULK ACOUSTIC RESONATORS



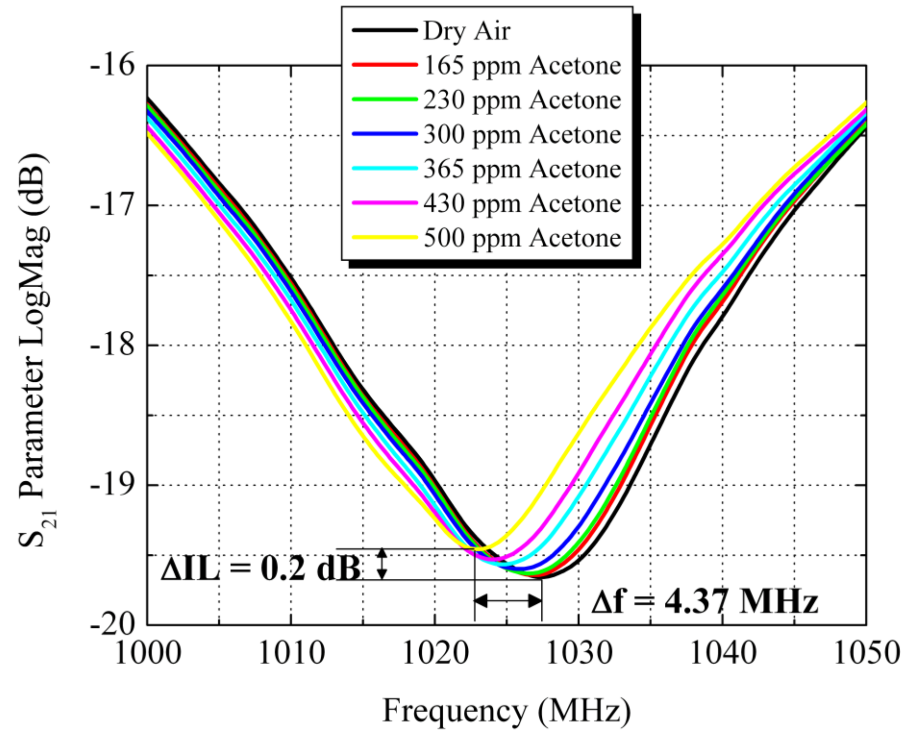


TFBAR

Acoustic device type	Mass sensitivity (cm^2/g)	Frequency range
QCM	10 – 20	5 – 30 MHz
SAW	200 – 400	50 – 1000 MHz
TFBAR	500 – 1000	1 – 20 GHz



TFBAR SENSOR AS PASSIVE DEVICE MEASURED BY NETWORK ANALYZER



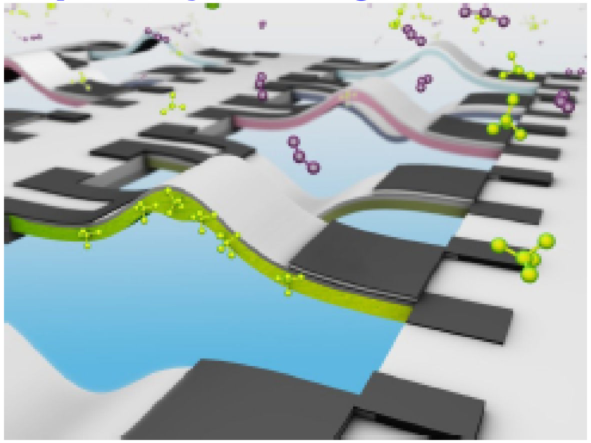
Thickness of 75wt.% SWCNTs-CdA LB Film = 28 nm
Cadmium arachidate (CdA) is Host-matrix
SWCNTs are fillers of NANOCOMPOSITE

M. Penza et al., IEEE Trans. Electr. Dev. 55-5 (2008) 1237

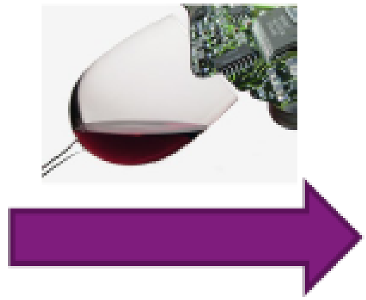
Type of Sensor: MEMS - MICRO ELECTRICAL MECHANICAL SYSTEMS

Towards a miniaturized MEMS e-nose

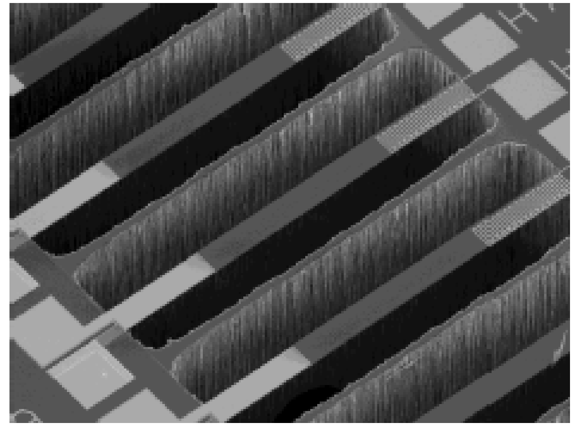
Frequency change induced by adsorbed mass onto individual cantilever

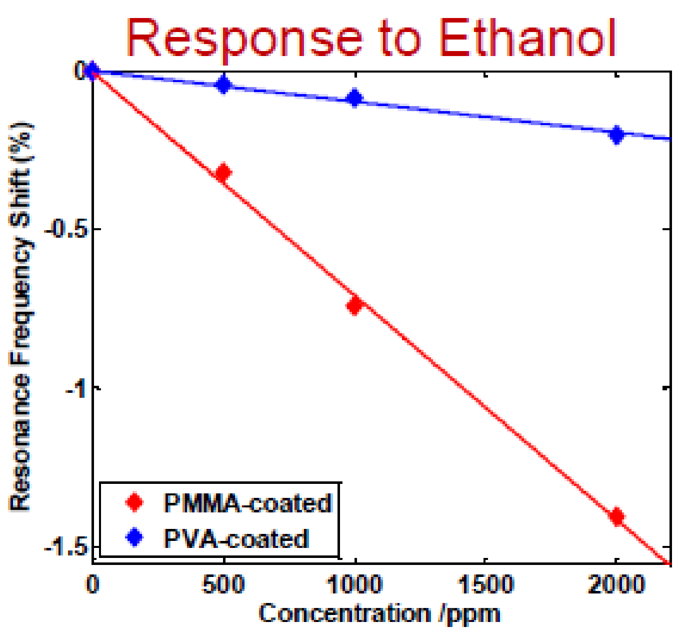


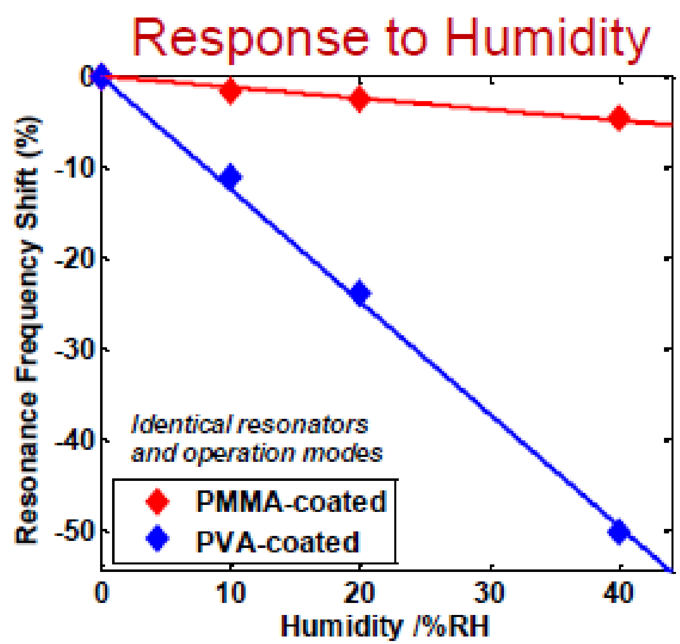
CONCEPT



REALITY



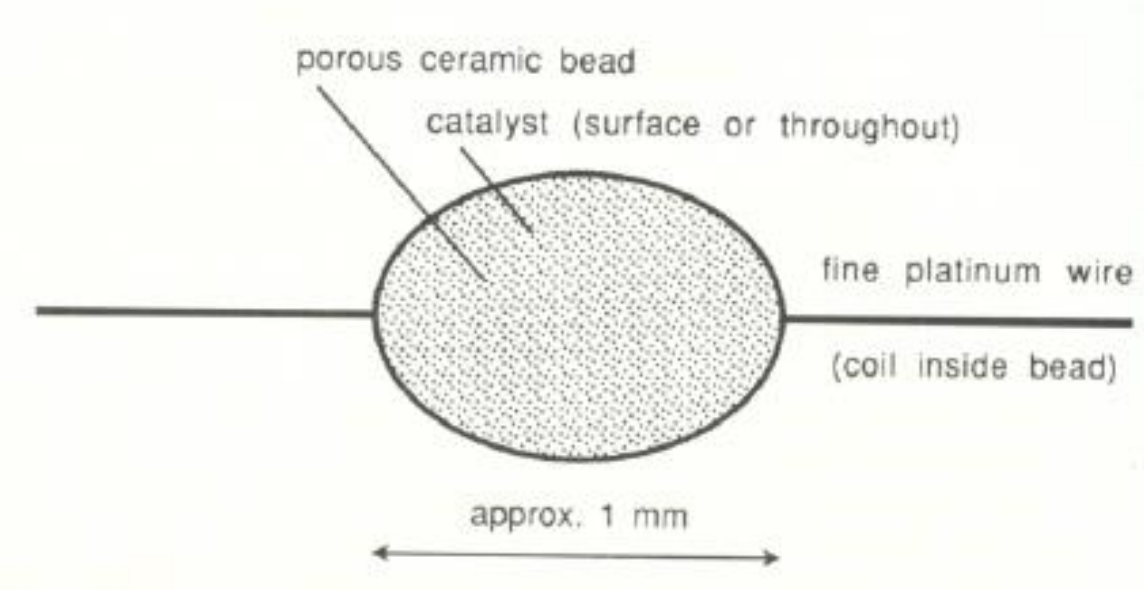




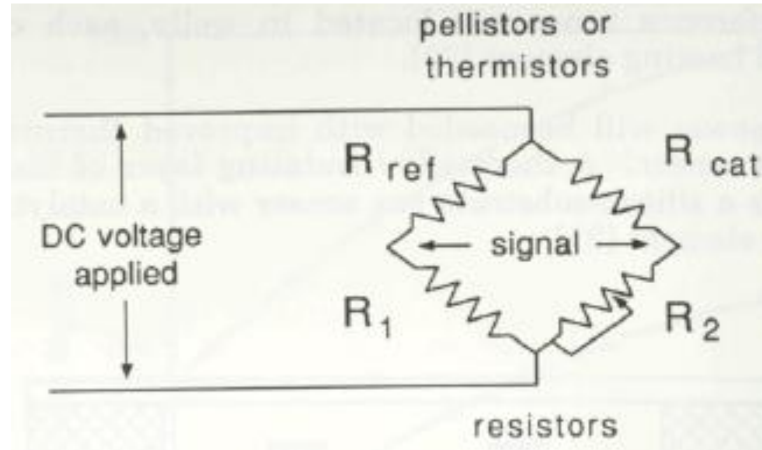
Courtesy by Sywert H. Brongersma from IMEC Holst-Centre

Type of Sensor: PYROELECTRIC or CATALYTIC

Outline of the pellistor heated-catalyst sensor



Wheatstone bridge for catalytic sensor

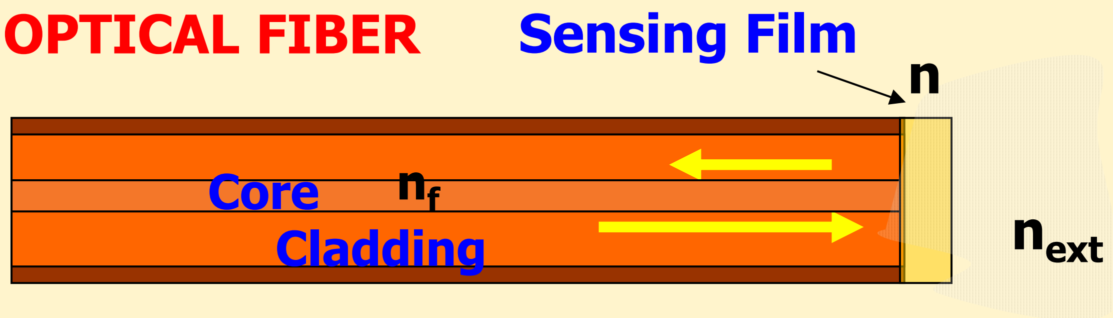


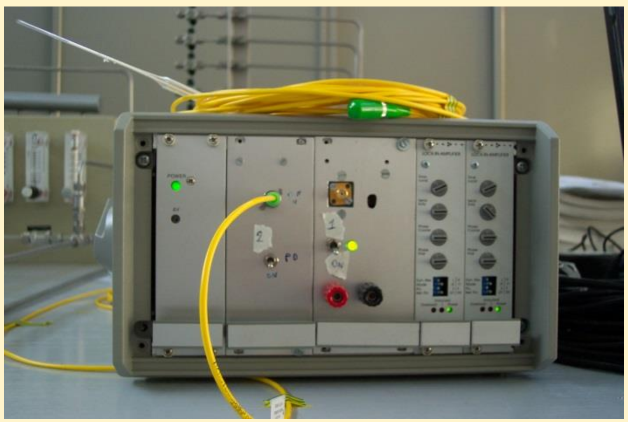
The pellistor is heated to about 500°C by passing electrical current through the Pt resistance wire. Any increase in temperature resulting from ***oxidation*** *of a gas to be detected on the Pt-doped surface of the bead causes a resistance change, which is measured by means of a Wheatstone bridge circuit.*

E. Allan Symons, Catalytic Gas Sensors, in Gas Sensors, G. Sberveglieri Ed., 1992 Kluwer Academic Publishers

Type of Sensor: OPTICAL FIBER

Optical Fiber Gas Sensors

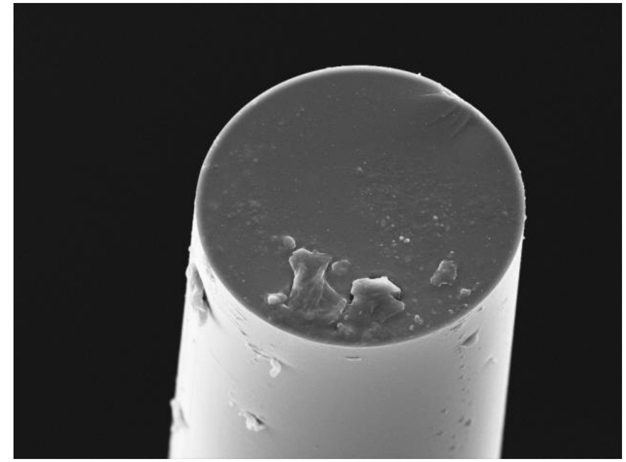




Refractometry

M. Consales, UNISANNIO (Italy)

M. Giordano, CNR-IMCB, (Italy)



overall diameter: 125 μm
core diameter: 6 μm

$$R = \left(\frac{n_f - n_m}{n_f + n_m} \right)^2$$

The sensor is based on the **Fresnel reflection** principle:
the **reflection coefficient R** is related to the difference between the medium *refractive index* n_m, the fiber optic *refractive index* n_f and the *incidence angle*.
In the case of a monomode fiber, the reflection coefficient **R** at the end of the **interface fiber-layer** can be expressed as above equation.

GAS SENSORS:
SENSOR PARAMETERS

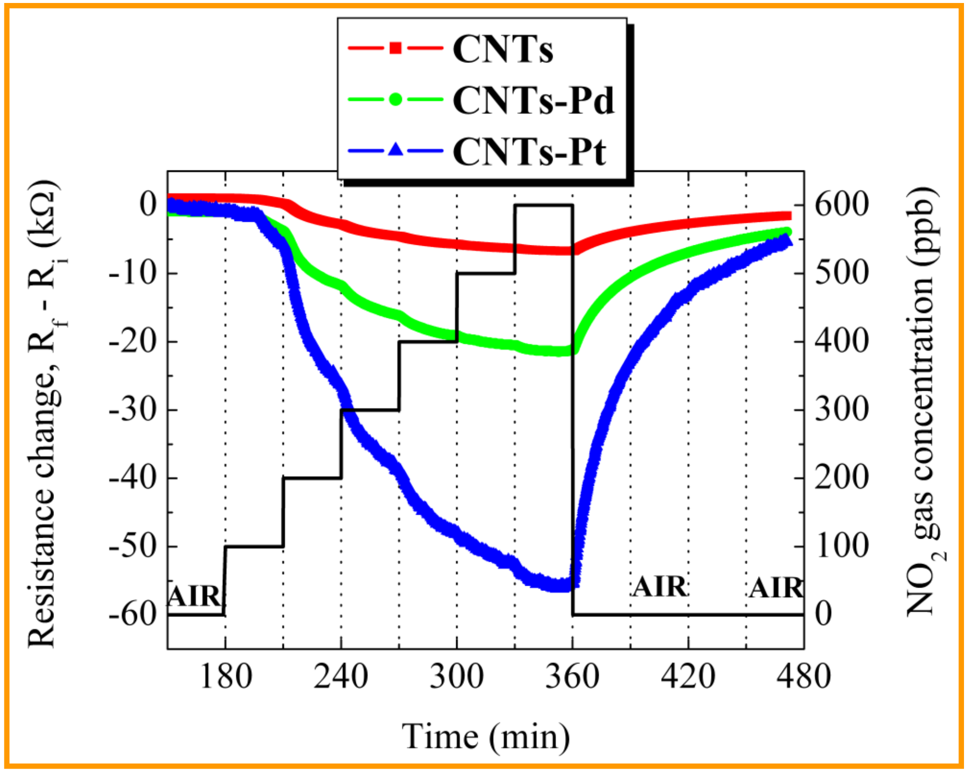
SENSOR PARAMETERS

Sensor Parameter	Figure of Merit
Response	**ΔR** (Ohm); **ΔR/R** (%); **R_i/R_f**; **ΔV** (V); **ΔI** (A); **V_i/V_f**; **I_f/I_i**; **ΔC** (F); **Δf** (Hz)
Sensitivity	**ΔR/c** (Ohm/ppm); **(ΔR/R)/c** (%/ppm); **Δf/c** (Hz/ppm); etc.
Response Time	**t_R** (sec or min)
Recovery Time	**t_C** (sec or min)
Limit of Detection	**LOD** (ppm or ppb)
Selectivity	Zero cross-sensitivity (*ideal case* !)
Reproducibility	Dispersion (%) of results in measurements under specific conditions
Repeatability	Dispersion (%) of results in repeated measurements
Stability & Drift	Attitude (% of full scale) to keep constant in time a metrological feature
Accuracy	Attitude (% dispersion) to give a result close to true value of a measurand
Resolution & Noise	Minimum *resolved* value of a measurand compared to a defined level of noise

R = Electrical Resistance; **I** = Current; **V** = Voltage; **C** = Capacitance; **f** = Frequency; **t** = time; **c** = gas concentration; **ppm** = part per million; **ppb** = part per billion

Sensor Parameter: RESPONSE

SENSOR RESPONSE: The output signal of the sensor stimulated by an external perturbation (e.g., gas concentration).
The Calibration Curve is defined as the functional relationship of the sensor response versus gas concentration.



EXAMPLES OF RESPONSE:

- **Chemoresistor: ΔR; $\Delta R/R$; R_i/R_f**
- **Capacitor: ΔC; $\Delta C/C$; C_i/C_f**
- **Piezoelectric Sensors: Δf; $\Delta f/f$; f_i/f_f**
- **Optical Sensors: ΔI; $\Delta I/I$; I_i/I_f**

Response of a CNT-based Chemiresistor towards NO_2 gas

M. Penza, et al., *Sensors and Actuators B*, 135 (1) (2008) 289-297

ATTENTION LEVEL = 100 ppb NO_2 - ALARM LEVEL = 200 ppb NO_2

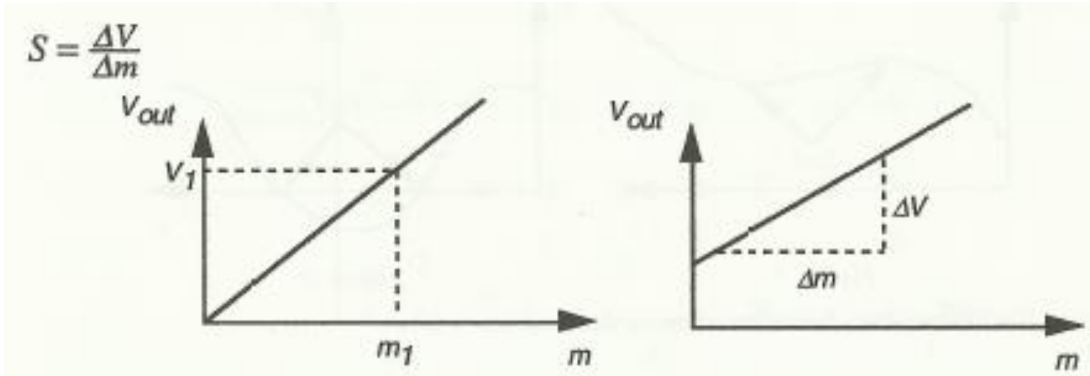
(Italian Regulations D.M. 15 April 1994 & Daughters)

Sensor Parameter: SENSITIVITY (1/2)

SENSITIVITY: In metrology and analytical chemistry, the sensitivity (S) is defined as the slope of the calibration curve. In other terms, the sensitivity is the response change of a sensor divided by the related variation of the input gas concentration.

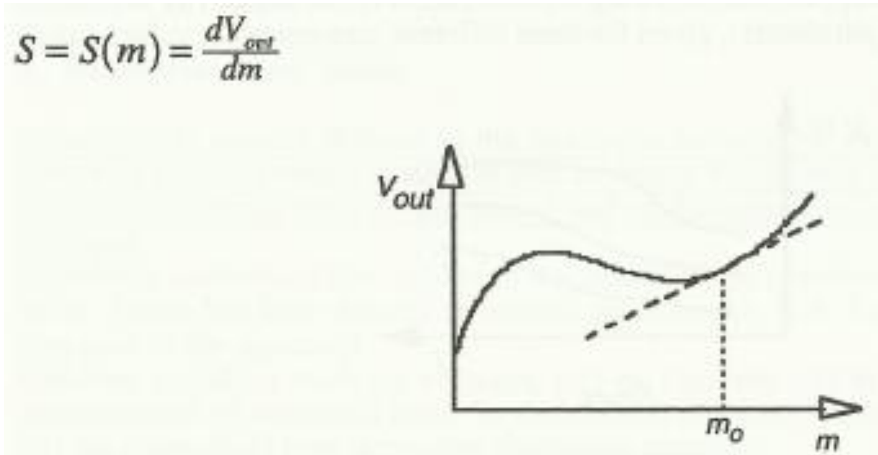
Sensor Sensitivity for Linear Calibration Curves:

Examples: %/ppm; mV/ppm; Hz/ppm; mA/ppb



Sensor Sensitivity for Not-Linear Calibration Curves:

Examples: Ohm/ppm; mV/ppb; Hz/ppm; µF/ppb



Sensor Parameter: SENSITIVITY (2/2)

SENSITIVITY: In metrology and analytical chemistry, the sensitivity (S) is defined as the slope of the calibration curve. In other terms, the sensitivity is the response change of a sensor divided by the related variation of the input gas concentration.

Other Figure of Merit:

Mean Sensitivity

$$S_m = \frac{1}{n}\sum_{i=1}^{n}\frac{(\Delta R/R)_i}{c_i}(\%/ppm)$$

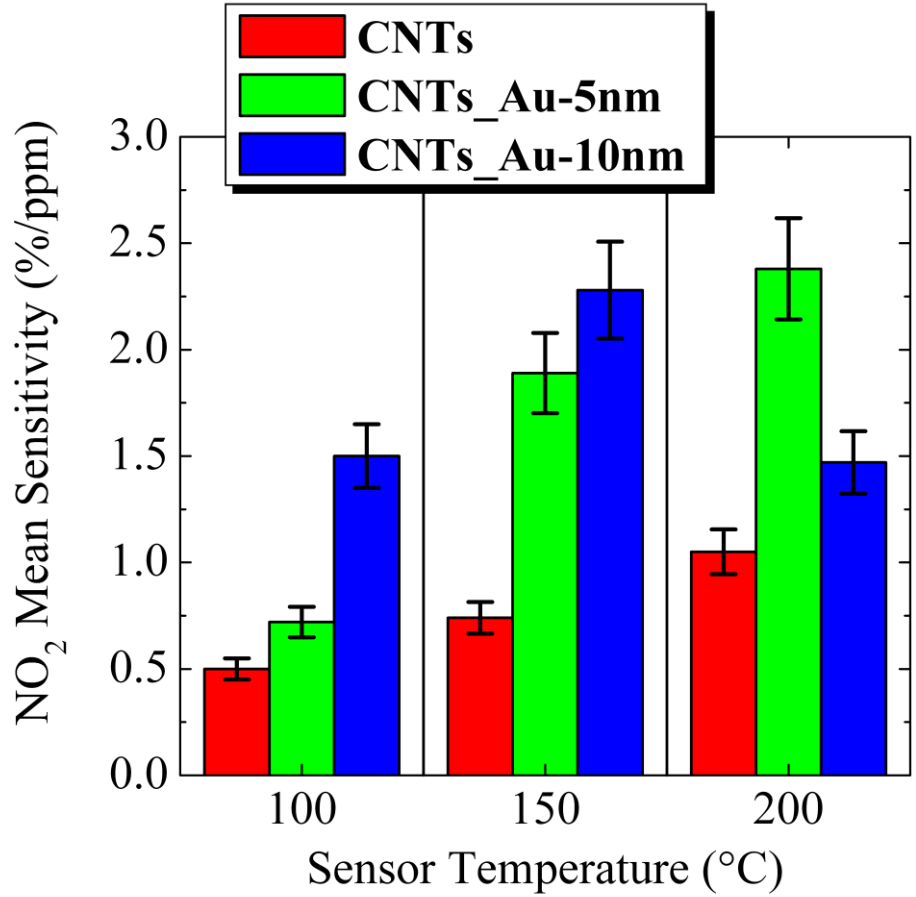
S_m = ***average sensitivity***

$\Delta R/R_i$ = ***sensor response***

c_i = ***gas concentration***

n = ***number of exposures***

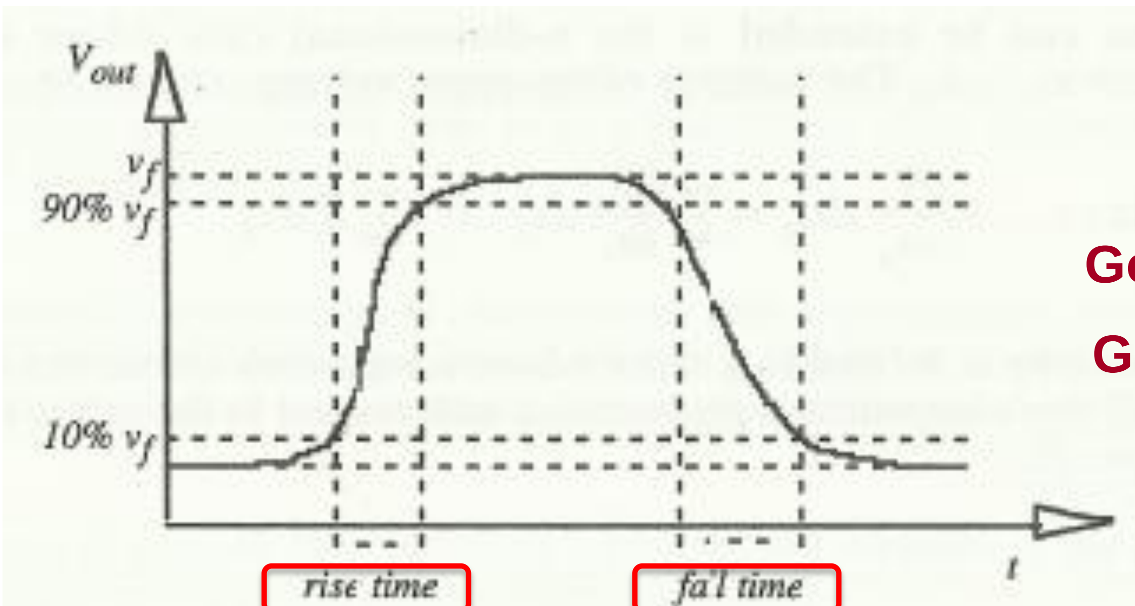
M. Penza, et al., *Sensors and Actuators B*, 140(1) (2009) 176-184.



Sensor Parameter: RESPONSE TIME & RECOVERY TIME

RESPONSE TIME: the time interval (RISE TIME) that the output response of a sensor goes through from 10 % to 90% of the final steady-state value upon reached stationary conditions.

RECOVERY TIME: the time interval (FALL TIME) that the output response of a sensor goes through from 90 % to 10% of the final steady-state value upon reached stationary conditions.



Good Response Time: < 10 sec

Good Recovery Time: < 60 sec

Sensor Parameter: LIMIT OF DETECTION (LOD)

LIMIT OF DETECTION: In metrology and analytical chemistry, the limit of detection (LOD) is defined as the minimum gas concentration (measurand) detected by a sensor (instrument) with a related output signal referenced to a fixed level of noise. The LOD is calculated as the *Minimum Detectable Value* (MDV) measured by a sensor, increased by *at least 3 times* (IUPAC requirement) related to measured *Noise* (N) level to be accurate, divided by *Sensitivity* (S) (slope of linear calibration curve).

$$LOD(ppm) = 3MDV / S$$

EXAMPLE of LOD Calculation for a Chemoresistor:

Noise = 10 Ohm; S/N = 3; MDV of a chemoresistor = 30 Ohm; S = 120 Ohm/ppm

LOD (ppm) = 3MDV /S = 30 Ohm / 120 Ohm/ppm = 0.25 ppm = 250 ppb

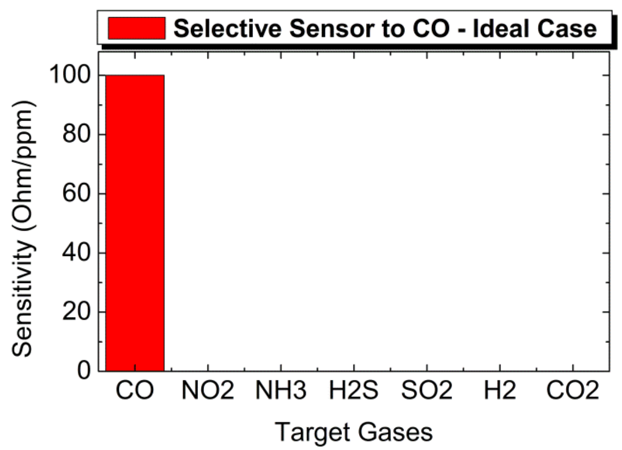
Sensor Parameter: SELECTIVITY

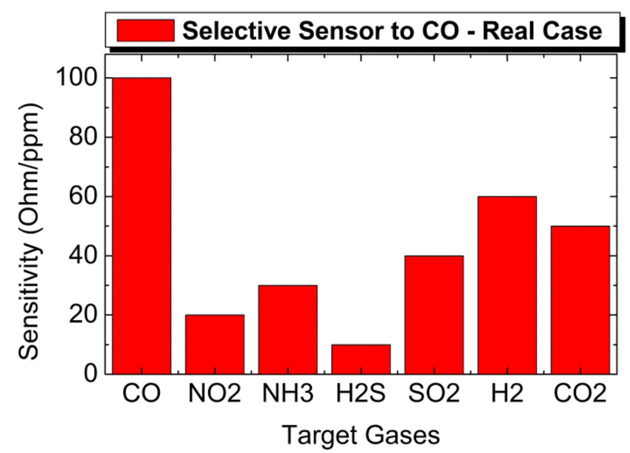
SELECTIVITY: degree of specificity of the response of a sensor to a given gas (target measurand) with *negligible cross-sensitivity* towards other interfering gases.

Usually, the gas sensitivity (S) of a sensor can be defined as a vector (V) with multiple components (V_i) depending on various tested gases (x_i) (*real case*):

$$dV_o = \frac{\partial V_o}{\partial x_1} dx_1 + \ldots + \frac{\partial V_o}{\partial x_n} dx_n = \sum_i \frac{\partial V_o}{\partial x_i} dx_i = \sum_i S_i dx_i$$

If the sensitivity towards a single given component (target gas) is dominant, then the sensor can be considered selective or specific (*ideal case*).





Sensor Parameter: REPRODUCIBILITY

REPRODUCIBILITY: degree of agreement among results of successive measurements of the same measurand when individual measurements are performed changing the following conditions: *method of measurement; instrument; usage conditions (temperature, pressure, etc.); time of measurement; operator; place of measurement; frequency of measurements*.

REPRODUCIBILITY can be expressed by a Standard Deviation (σ) as a Dispersion (%) of the results in the reproduced measurements.

$$\sigma = \sqrt{\frac{1}{n-1}\sum_{i=1}^{n}(x_i - \bar{x})^2}$$

x_i represents the result of the $i-th$ measurement

$\bar{x}$ represents the arithmetic average of n measurements

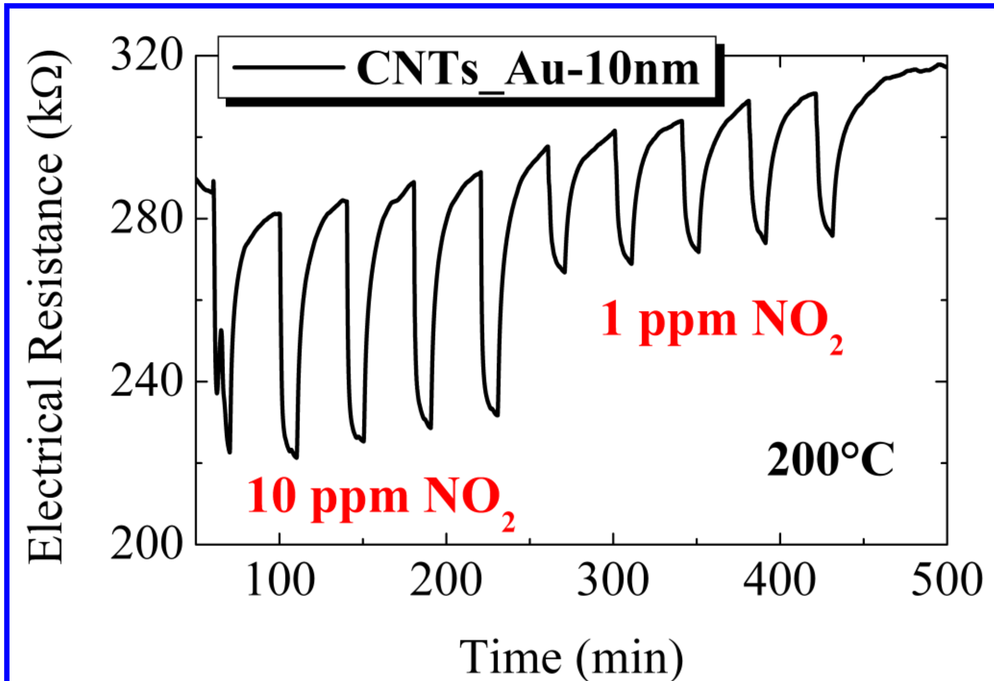
Good Reproducibility:
σ < 10%

A. D'Amico and C. Di Natale, IEEE Sensors Journal, Vol. 1, N. 3, October 2001, pp. 183-190

Sensor Parameter: REPEATABILITY

REPEATABILITY: degree of agreement among results of successive measurements of the same measurand under specific conditions: ***same method of measurement; same instrument; same usage conditions (temperature, pressure, etc.); time of measurement; same operator (observer); same place of measurement; frequency of measurements*****.**

REPEATABILITY can be expressed by a Standard Deviation (σ) as a Dispersion (%) of the results in the repeated measurements.



D = Coefficient of Variation (%)

SD = Standard Deviation; M = Mean

The LOWER D, the BETTER REPEATABILITY

	SENSOR CNTs_Au-10nm		
GAS CONC.	200 ppb NO_2	1 ppm NO_2	10 ppm NO_2
$D = (SD / M)\%$	12.1 %	3.08 %	1.50 %

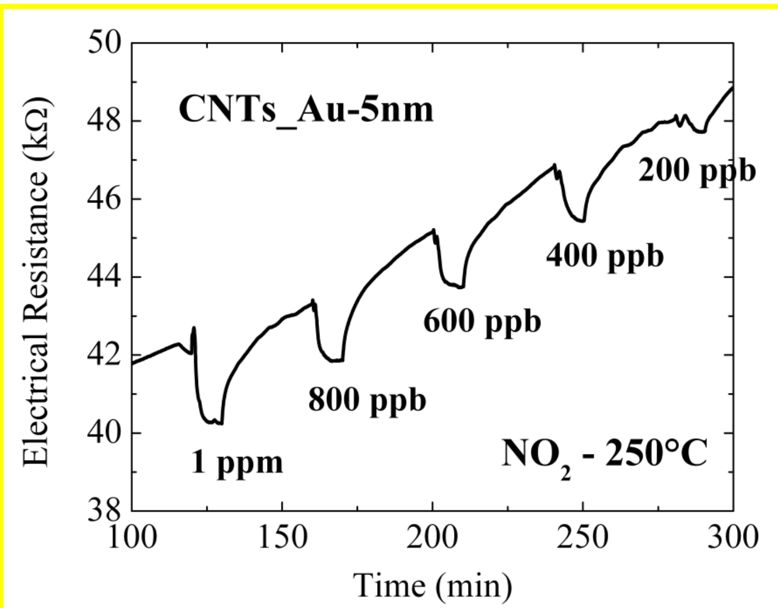
M. Penza et al., Sens. and Actuators B 140. 2009, 176-184

Sensor Parameter: STABILITY & DRIFT

STABILITY: Attitude of a sensor to maintan constant in the time its metrological characteristics (i.e., gas response), or as a function of other foreign parameters as external perturbations.

It can be expressed as data dispersion (%) related to full scale.

DRIFT: Slow time variation of a metrological feature (i.e., baseline) with unpredictable statistics. Instabilities of sensing material (*ageing effects*) and ambient interactions (*temperature, humidity*) are the main causes of changes of the overall performance (i.e., sensor response) in the device.



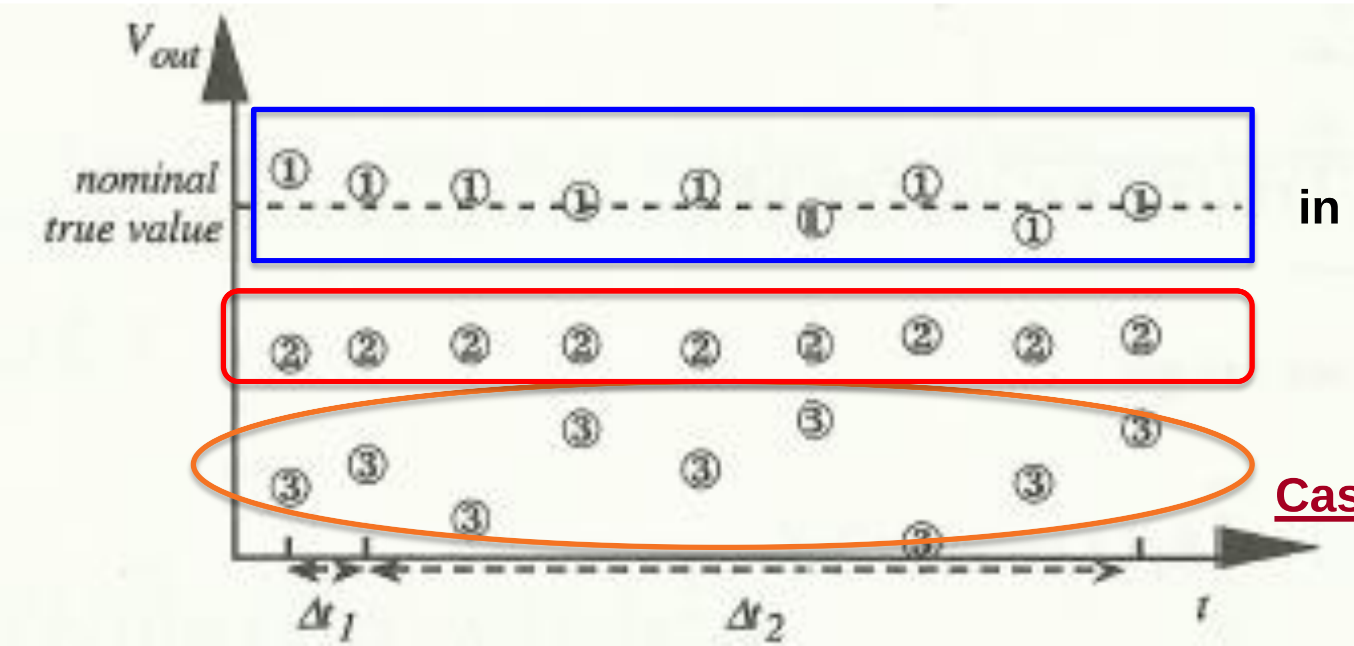
Drift of the Baseline of the Au-modified CNT sensor in the period of ca. 3 hours

NO_2 detection at gas concentration ppb level

M. Penza et al., Journal of Sensors, Vol. 2008, ID107057.

Sensor Parameter: ACCURACY

ACCURACY: Attitude of a sensor (instrument) to give an indication *close to the true value* of the measurand under test. The concept is clarified as follows:



Case 1: sensor Accurate in the limit of standard deviation

Case 2: sensor Repeatable but not Accurate

Case 3: sensor neither Repeatable not Accurate

A. D'Amico, C. Di Natale, A. Taroni, *Sensors Parameters*, in Proceedings of the 1st European School on Sensors (ESS'94).

Sensor Parameter: RESOLUTION & NOISE

RESOLUTION & NOISE: RESOLUTION is usually defined as the minimum meaningful value of a measurand that a sensor is able to detect. Resolution, in principle, is limited by the NOISE occurring both on the sensor (*active material*) and electronics (*amplifier*) used to readout the sensor response.

Most common kinds of Noise sources

Type of noise	Current Spectral Density $S_i(f)$
Thermal (Johnson)	$4kTG$
Generation - Recombination Burst	$A_1 \frac{\tau^2}{1+4\pi^2\tau^2 f^2}$
Shot	$2e\bar{i}$
Flicker	$A_2 \frac{\bar{i}^{\gamma}}{f^{\alpha}}$

A. D'Amico, C. Di Natale, A. Taroni, *Sensors Parameters*, in Proceedings of the 1st European School on Sensors (ESS'94).

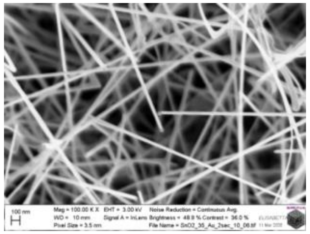
Roadmap of the R&D on Solid-State Gas Sensors

Year	Type of Sensor	Investigator(s)	Comments/References
1953	Surface modifications of a semiconductor by a cycle wet/dry of a gas	W. Brattain, J. Bardeen	Bell. Syst. Tech. J., 32 (1953) 1
1962	Thin film gas sensor based on semiconducting metal oxides	T. Seyama	Analytical Chemistry 34 (1962) 1502
1962	Gas sensor based on semiconducting oxide	N. Taguchi	Jpn. Patent 45-38200, 1962
1964	Quartz piezoelectric sensor for gas/vapor detection	W. H. King	Analytical Chemistry 36 (1964) 1735
1967	Glucose sensor	S.J. Updike *et al.*	Nature 214 (1967) 986
1970	Gas sensor based on semiconducting oxide (SnO_2)	K. Taguchi	US-Patent 3631436 (1970)
1970	Sensor based on Ion-Sensitive Field Effect Transistor (ISFET)	P. Bergveld	IEEE Trans. Biomed. Eng. BM-17 (1970) 70
1975	Gas sensor based on semiconducting polymers	J. Janata *et al.*	Analytical Chemistry 47 (1975) 2238
1975	Sensor MOSFET with Palladium gate for detection of hydrogen	I. Lundstrom *et al.*	Appl. Phys. Lett. 26 (1975) 55
1978	Gas Sensor based on p-type semiconductor	J. R. Stetter	J. Colloidal Interfaces Science 65 (1978) 432
1979	Study of sensing mechanisms of semiconducting gas sensors	N. Yamazoe *et al.*	Surface Science 86 (1979) 335
1980	Gas Sensor based on optical fiber coated by senstive dye	J. I. Peterson *et al.*	Science 224 (1980) 123
1982	SAW quartz sensor coated with Palladium film for hydrogen detection	A. D'Amico *et al.*	Appl. Phys. Lett. 41 (1982) 300
1984	SAW gas and vapour sensor based on gravimetry	H. Wohltjen	Sensors and Actuators 5 (1984) 307
1985	Study of sensing mechanisms at surface and bulk of semiconductors	W. Gopel	Surface Science 20 (1985) 9
1987	SAW sensor at high frequency with polymers coatings for vapor/gas sensing	R. M. White *et al.*	IEEE Tr. Ultr. Ferr. Freq. Contr. 34 (1987) 162
1991	Discovery of Carbon Nanotubes	S. Iijima	Nature 354 (1991) 56
1991	Multisensor system for detection of vapors and odours by pattern recognition	J. W. Gardner	Sensors and Actuators B 4 (1991) 109
1992	Gas sensor based on SnO_2 semiconducting thin-film prepared by RGTO	G. Sberveglieri	Sensors and Actuators B 6 (1992) 239
1995	Electronic Nose based on thin-film sensors for wine aroma profile	C. Di Natale *et al.*	8° Conference EUROSENSORS, Stockolm
1996	Electronic Nose based on polymeric film sensors for chemical detection	K. C. Persaud *et al.*	Handbook Biosensors and Electronic Noses
2000	Sensor based on carbon nanotubes for detection of NO_2 and NH_3	H. Dai *et al*	Science 287 (2000) 622
2001	Nanosensor based on Silicon nanowire for detection of chemical and biological species	C.M. Lieber *et al.*	Science 293 (2001) 1289
2002	Gas sensor based on a SnO_2 semiconducting nanobelt	G. Sberveglieri *et al.*	Appl. Phys. Lett. 81 (2002) 1869
2003	Gas sensor based on carbon nanotubes for gas and vapour detection	M. Meyyappan *et al.*	Nano Letters 3 (2003) 929
2005	Bio-sensors based on carbon nanotubes for biomedical applications	J. T.-W. Yeow *et al.*	IEEE Trans. NanoBioscience 4 (2005) 180
2007	Development of monocrystalline nanowires for functional applications	C.M. Lieber e Z.L. Wang	MRS Bullettin 32(2) (2007) 99
2009	Nanoelectronic Nose based on CNT sensor array for gas discrimination	C. Zhou *et al.*	Nanotechnology 20 (2009) 125503
2010	Detection of individual gas molecules adsorbed on graphene	K. Novoselov, A. Geim Nobel Prize in Physics	*Nature Materials 6 (2007) 652-655*

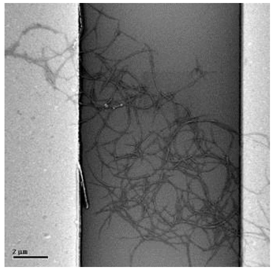
History and *Roadmap* of Carbon Nanotubes Gas Sensors

YEAR - AUTHOR	TYPE OF SENSOR AND COMMENTS	REFERENCES
1991 - **S. Iijima**	Multiwalled Carbon Nanotubes were discovered	*Nature 354 (1991) 56*
1993 - S. Iijima	Singlewalled Carbon Nanotubes were engineered	*Nature 363 (1993) 603*
2000 - H. Dai	First SWCNT gas sensor for NO_2 and NH_3 gas detection	*Science 287 (2000) 622*
2000 - P.G. Collins	SWCNT gas sensor for O_2 gas detection	*Science 287 (2000) 1801*
2001 - H. Dai	Functionalized CNT gas sensor for H_2 gas detection	*Adv Mater 13 (2001) 1384*
2003 - L. Valentini	CNT-based Chemiresistor for NO_2 gas detection at 165°C	*Appl. Phys. Lett. 82 (2003) 961*
2003 - T. Someya	SWCNT-based FET for vapour detection	*Nano Lett. 3 (2003) 877*
2003 - M.Meyyappan	CNT gas sensor for vapor/gas detection at room temperature	*Nano Lett. 3 (2003) 929*
2005 - J. Yeow	Review on CNT Biosensors for mediacal applications	*IEEE Trans. NanoBiosci. 4 (2005) 180*
2007 - CM Lieber and ZL Wang	Singlecrystalline Nanowires for functional applications	*MRS Bulletin 32 (2007) 99*
2007 - M. Penza	Effect of growth-catalysts on sensitivity of CNT gas sensors	*Appl. Phys. Lett. 90 (2007) 103101*
2008 - E. Llobet	Carbon nanotube-TiO_2 hybrid films for detecting O_2 traces	*Nanotechnology 19 (2008) 375501*
2009 - C. Zhou	Electronic Nose CNT sensor-array for gas discrimination	*Nanotechnology 20 (2009) 125503*
2010 - K. Novoselov, A. Geim Nobel Prize in Physics	**Detection of individual gas molecules adsorbed on graphene**	***Nature Materials 6 (2007) 652-655***

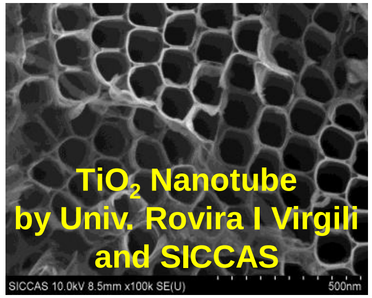
Selected Examples of Gas Sensors and Sensor Systems



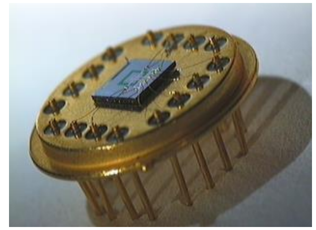
Metal oxide (SnO_2) Nanowires nets by Univ. of Brescia



Carbon Nanotubes by Ames NASA



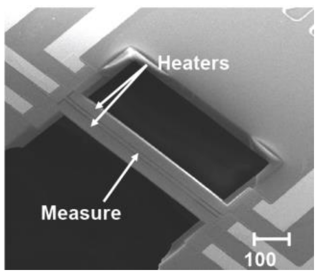
TiO_2 Nanotube by Univ. Rovira I Virgili and SICCAS



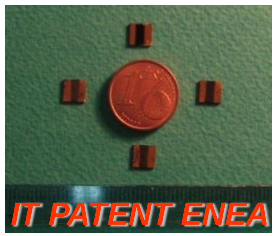
GasFET by EPFL, CH

UNITEC srl, ETL3000
multi-component outdoor air quality monitor

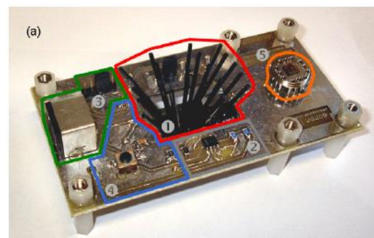
AEROQUAL, AQM 60
Air Quality Sensors Station



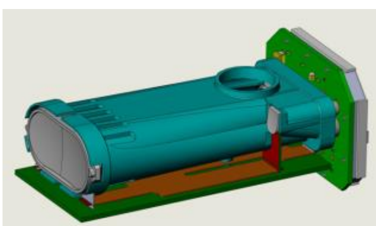
Cantilever Sensor by DTU, DK



Carbon Nanotube Gas Sensors

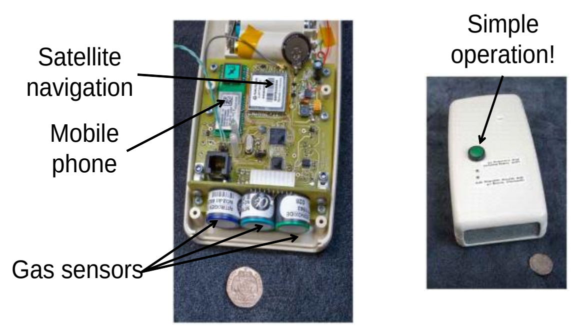


Autonomous Gas Sensor System by IREC and Univ. of Barcelona



SenseAir SA,
A Robust Low-Cost NDIR Sensor Platform for sub-ppm Gas Detection

Sensor units components



400 gm (incl. batteries)

An Octocopter, the first platform on which we (*Max Planck Institute for Biogeochemistry, Jena, Germany*) tested a measurement sensor package for air quality sensors.

CURRENT STATUS in AIR QUALITY SENSORS

European Commission

Michel Gerboles, JRC-Ispra, IES

Fixed measurements: definition

'fixed measurements' means measurements taken at fixed sites to determine the levels in accordance with the relevant *Data Quality Objectives* (DQO);

Fixed measurements are mandatory in zones and agglomerations where the upper assessment thresholds are exceeded.

AQD: European DIRECTIVE 2008/50/EC on ambient air quality and cleaner air for Europe, art. 2

CURRENT STATUS in AIR QUALITY SENSORS

European Commission

Michel Gerboles, JRC-Ispra, IES

AQD: Data Quality Objectives (DQO)

	SO_2, NO_2/NOx, CO	Benzene	O_3
Uncertainty for **fixed measurements**	15 %	25 %	15 %
	Fluoresc., chemil., NDIR	automatic GC or pumped sampling	UV photometry
	demonstration of equivalence would be mandatory to use micro-sensors		

CURRENT STATUS in AIR QUALITY SENSORS

European Commission

Indicative methods: definition

'indicative measurements' means measurements which meet *data quality objectives* that are less strict than those required for *fixed measurements*;

AQD: European Directive 2008/50/EC on ambient air quality and cleaner air for Europe, art. 2

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CURRENT STATUS in AIR QUALITY SENSORS

European Commission

AQD: Data Quality Objectives (DQO)

	SO_2, NO_2/NO/NOx, CO	Benzene	O_3
Uncertainty for **fixed measurements**	15 %	25 %	15 %
Uncertainty for **indicative measurements**	**25 %**	**30 %**	**30 %**
	diffusive samplers, ***micro-sensors***		

Michel Gerboles, JRC-Ispra, IES

New Sensor Technologies

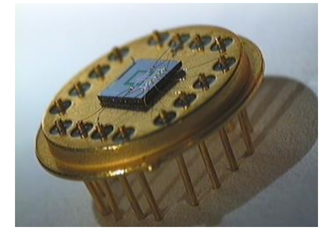
- **Miniaturisation of MOX**: huge number of publications on nano particles, nano-wire, carbon nanotubes: **no commercial sensors yet**
- **Graphene sensors** (material with low resistance able to enhance sensitivity) - **no commercial sensors yet**
- **Chemical filter** directly coated on the sensing layer to avoid cross-sensitivity (NO_2 and O_3)
- **Low-cost and Low-power Gas Sensors** (Alphasense Ltd, SenseAir SA, UST GmbH, SGX-Sensortech SA, Sensichips srl, Figaro Inc, FIS Inc, etc.) in integrated air-quality stations (Unitec, Aeroqual, Contec, Libelium, Environnement, etc.), personal light badge

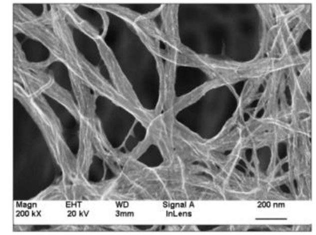
European Policy for the use of sensors

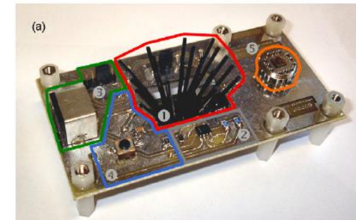
- **Micro-sensors**:
- - **for now**: not mentioned, not foreseen in European legislation for regulatory purposes
- - **European Members States** shall demonstrate that the Data Quality Objective for Indicative Methods is met (***national projects***).

- **For now**, the European Commission mainly observes the results of some Research projects related to micro-sensors: *MACPoll*, *AIRMONTEC*, *FP7- ENV.2012.6.5-1* (air quality monitoring in a "Smart City" context with community involvement, *S3-EURUSSIA*, ***COST Action TD1105 EuNetAir***, etc. …)

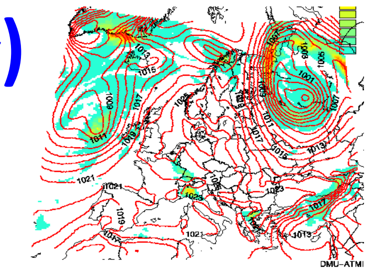
CONCLUSIONS



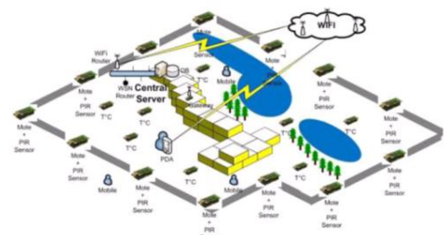




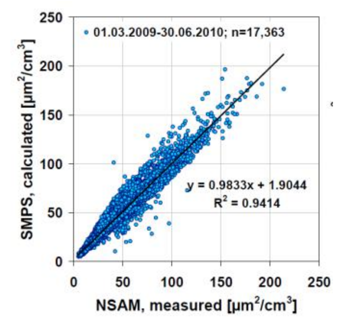
- Nanomaterials for AQC sensors
- Low-cost Gas Sensors
- Low-power Sensor-Systems
- Wireless Technology (*Environmental Sensors Network*)



- Air Quality Modelling



- Environmental Measurements
- Standards and Protocols



- Guidelines for Best Coupling Gas/Transducer
- Personal Exposure and Health Assessment

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REFERENCES

- Lloyd A. Currie, *Nomenclature in evaluation of analytical methods including detection and quantification capabilities*, 1995 IUPAC, **Pure & Applied Chemistry**, Vol. 67, No. 10 (1195) 1699-1723.
- A. D'Amico, C. Di Natale, A. Taroni, *Sensors Parameters*, in Proceedings of the 1st European School on Sensors (ESS'94): *Sensors for Domestic Applications*, Castro Marina (Lecce), Italy - September 12-17, 1994, pp. 3-13.
- A. D'Amico and C. Di Natale, *A contribution on some basic definitions of sensors properties*, **IEEE Sensors Journal**, Vol. 1, N. 3, October 2001, pp. 183-190.
- G. Sberveglieri, *Gas Sensors*, Kluwer Academic Publishers, 1992.
- J. W. Gardner and P. N. Bartlett, *Electronic Noses: Principles and Applications*, Oxford Science Publications, 1999.
- R. Pallas-Areny and J. G. Webster, *Sensors and signal conditioning*, Wiley, 1991.
- R. W. Cattrall, *Chemical Sensors*, Oxford Science Publications, 1997.
- C. K. Ho, A. Robinson, D. R. Miller and M. J. Davis, *Overview of sensors and needs for environmental monitoring*, **Sensors** 5 (2005) 4-37.
- W. Gopel, J. Hesse, J.N. Zemel Editors, *Sensors - A comprehensive Survey, Chemical and Biochemical Sensors*, Vol. 2 and Vol. 3. VCH, 1992.
- M. Penza, *Carbon nanotubes for gas sensing applications: principles and transducers*, Chapter 9 (pp. 333-468) in *Carbon Nanomaterials for Gas Adsorption* (M.L. Terranova, S. Orlanducci, M. Rossi Eds.). Pan Stanford Publishing, 2013.
- M. Gerboles, EC JRC-Ispra, Invited Talk at COST Action TD1105 Rome meeting, 4-6 Dec. 2012.

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

EuNetAir

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

cost

EUROPEAN COOPERATION IN SCIENCE AND TECH

TRAINING SCHOOL
on Environmental Technologies and Air-Quality Monitoring

Barcelona, 13 - 15 June 2013

UNIVERSITAT de BARCELONA (UB), MIND-IN2UB - Departament d'Electrònica
c/ Martí i Franquès, 1 - E-08028 Barcelona, Spain
and CSIC-IDAEA, c/ Jordi Girona, 18 - E-08034 Barcelona, Spain

Green Week 2013 - Brussels 4-7 June

Green Week 2013 satellite event

http://ec.europa.eu/environment/greenweek/







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- **CONSORTIUM COST Action TD1105 EuNetAir**

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- **<u>PON1 BAITAH</u> -** *Methodology and Instruments of **B**uilding **A**utomation and **I**nformation **T**echnology for pervasive models of treatment and **A**ids for domestic **H**ealthcare*

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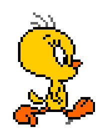

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