Micromachined gas sensor and integrated optical circuit

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***JPA SA**

Micromachined Gas Sensors with nanostructures SnO_2 films

Outline

* Gas sensor Architecture

* Tecnological Process

* Deposition Thin Film Methods

* Structural Characterization of the film

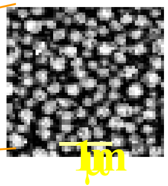
Functional Characterization of the sensor

* Applications of MEMS gas sensors

gas monitors & e-noses

Summary and perspectives

Sensor microstructure



1 mm

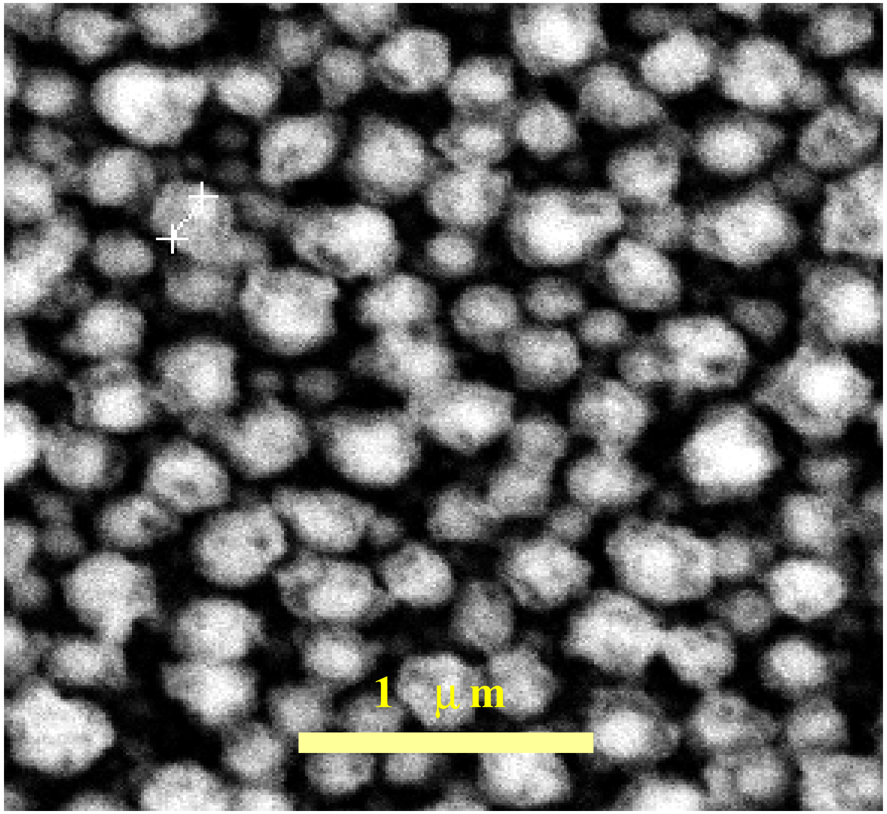
- Semiconductor chemical sensors: transduce chemical composition change in conductivity change
- Constant voltage (1 Volt) → current change

- *IC compatible fabrication process;*
- *Low thermal conductivity of the Si_3N_4/SiO_2 membrane;*
- *Reduced thermal mass of the device;*

Rise Time and Recover Time$\cong$ 30 ms

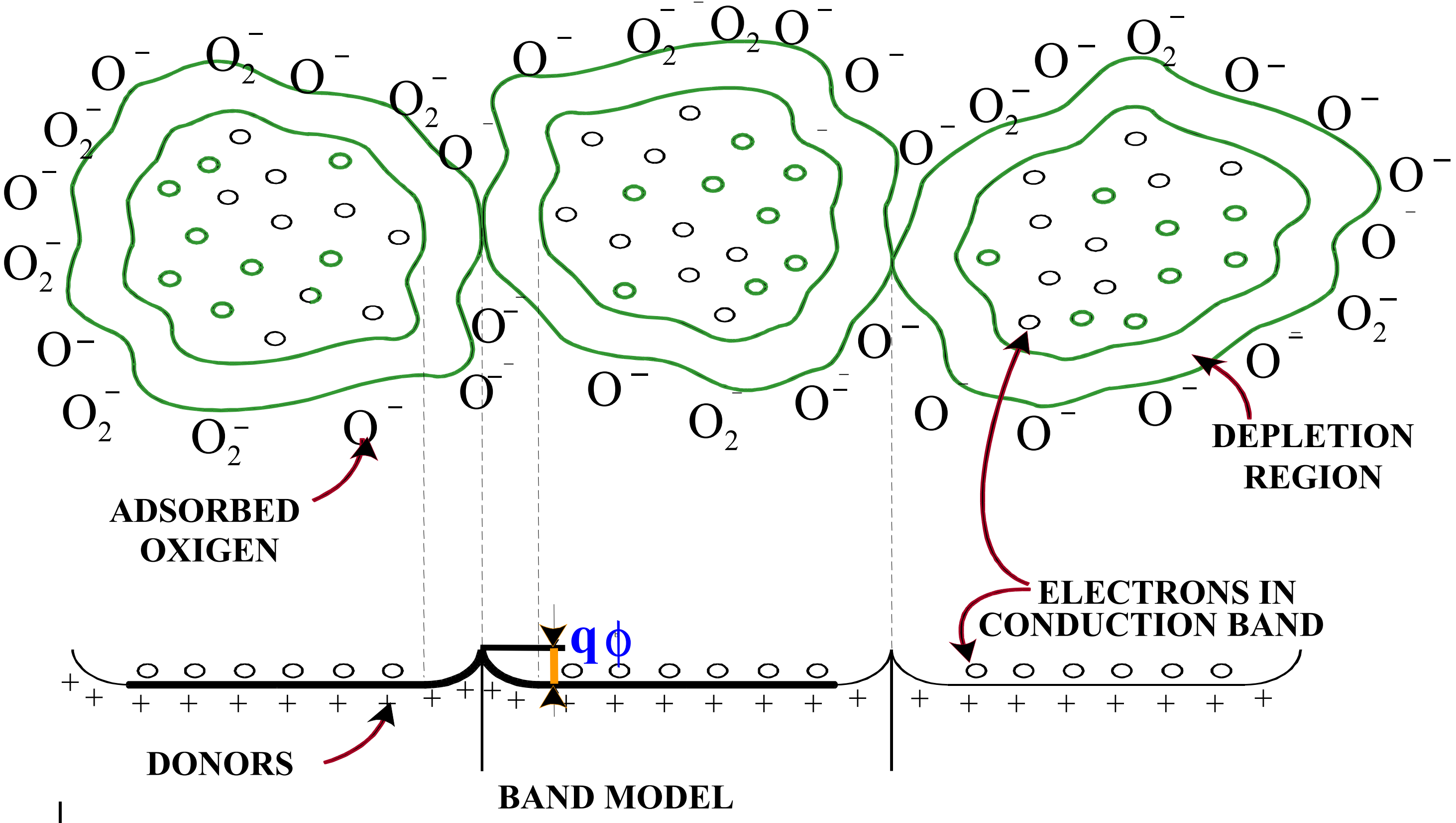
(drawing: courtesy of S. Nicoletti , IMM-CNR Bologna Italy)

SEM micrograph of 200nm thick SnO_2 film



Conduction model for polycrystaline semiconductors

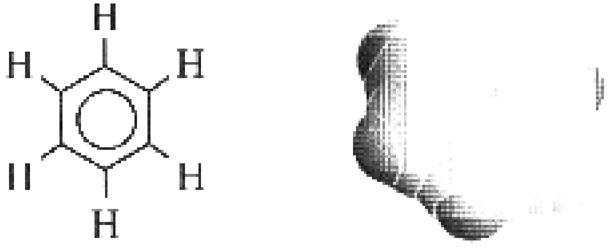
$$CO + O \longrightarrow CO_2 + e^-$$



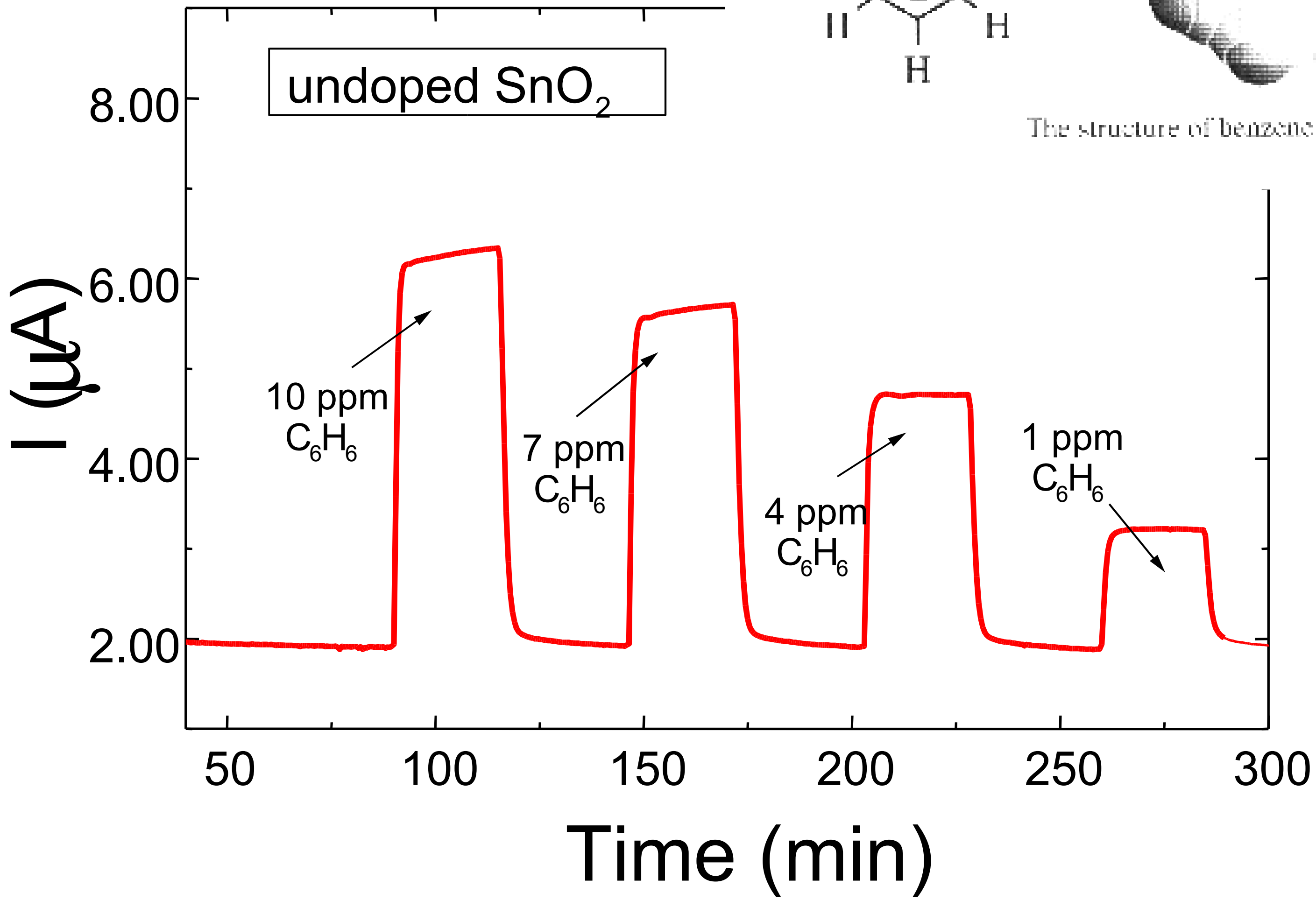
- The sensitive film is constituted of a nanostructured polycrystalline grain-structured Tin Oxide layer (SnO_2)
- Gases interact with the oxygen adsorbed on the film surface;

Red/Ox Reactions ⇔ Variation on the conductibility of the film

Conductance change of 200 nm thick undoped SnO_2 film when exposed to different benzene concentrations (1÷10 ppm range).



The structure of benzene.

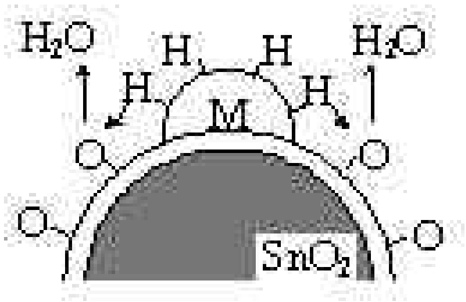


Enhanced selectivity to different gases

- **device operates via resistivity changes**
- **gas molecules carry out a reduction/oxidation process on grains surfaces, increasing/ reducing the resistance of the film**
- **device operates at 200 to 500 °C**
- **selectivity could be modified for a particular gas species doping the metallic oxide with different elements (Pt , Pd , Au, V, etc...)**
- **Oxygen presence required for normal operation**

Sensitivity increase by adding a catalyst

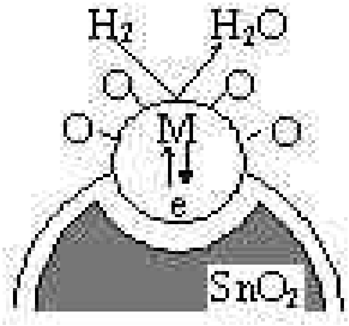
role of the metal



activation and spill-over of the gas

change of the concentration of the adsorbed oxygen

Pt



donor and acceptor of electrons

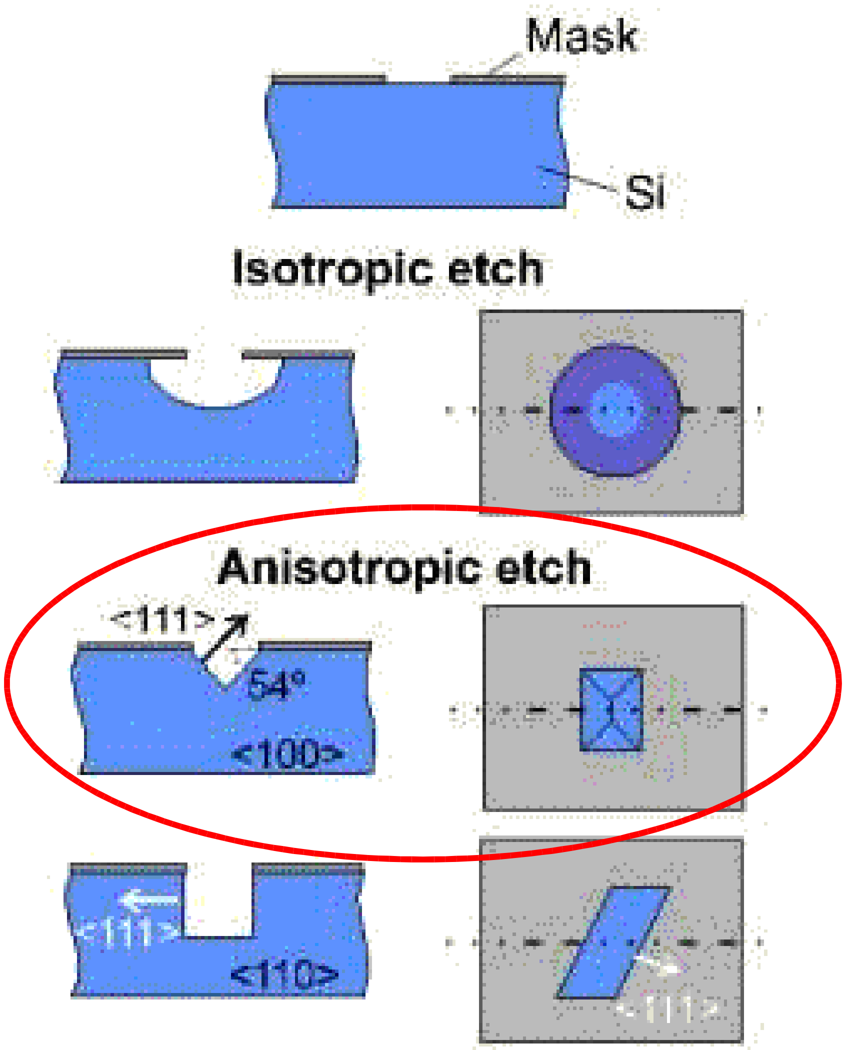
metal oxidation change of state

Ag_2O, PdO

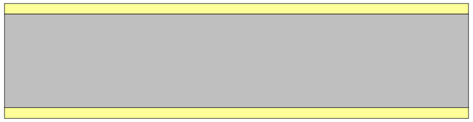
N.Yamazoe, *Sensors and Actuators B*, Vol. 4, pag. 7 (1991)

Device Structure

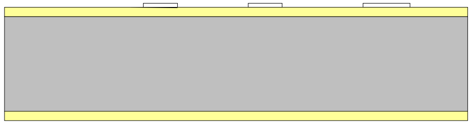
Bulk Micromachining



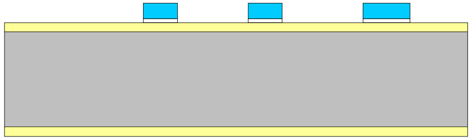
- Isotropic chemical etching
- Chemical Reactives for Si anisotropic: KOH, EDP
- etch stop is done using a film highly doped or Si_3N_4



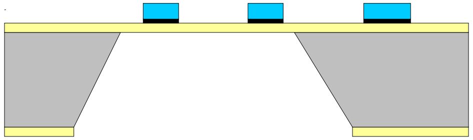
Deposition of 200 nm of Si_3N_4 on both sides of the silicon wafer



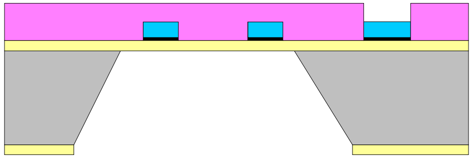
Evaporation of Ti thin film for adhesion



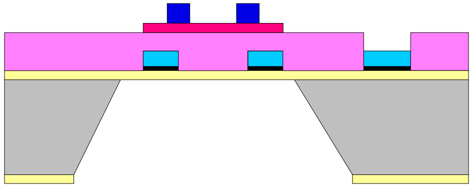
Evaporation and patterning of 300 nm Pt films for the heating resistor and the temperature sensor



Micromachining of the back of the Si wafer, in KOH - DI water solution at 80°C, leaving a freestandingSi_3N_4 membrane

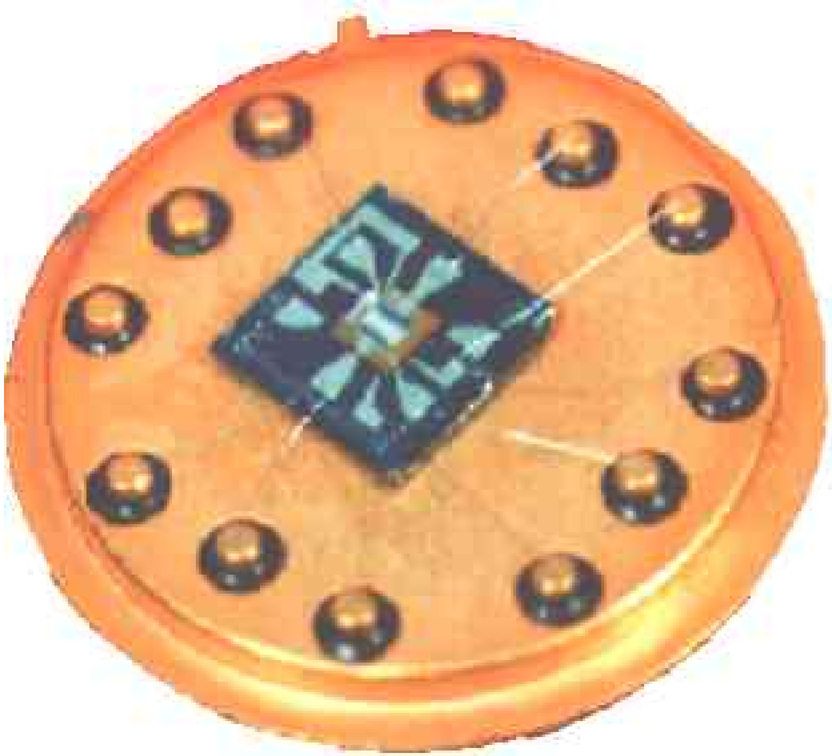


SOG film spinning for insulation of sensitive film and heater



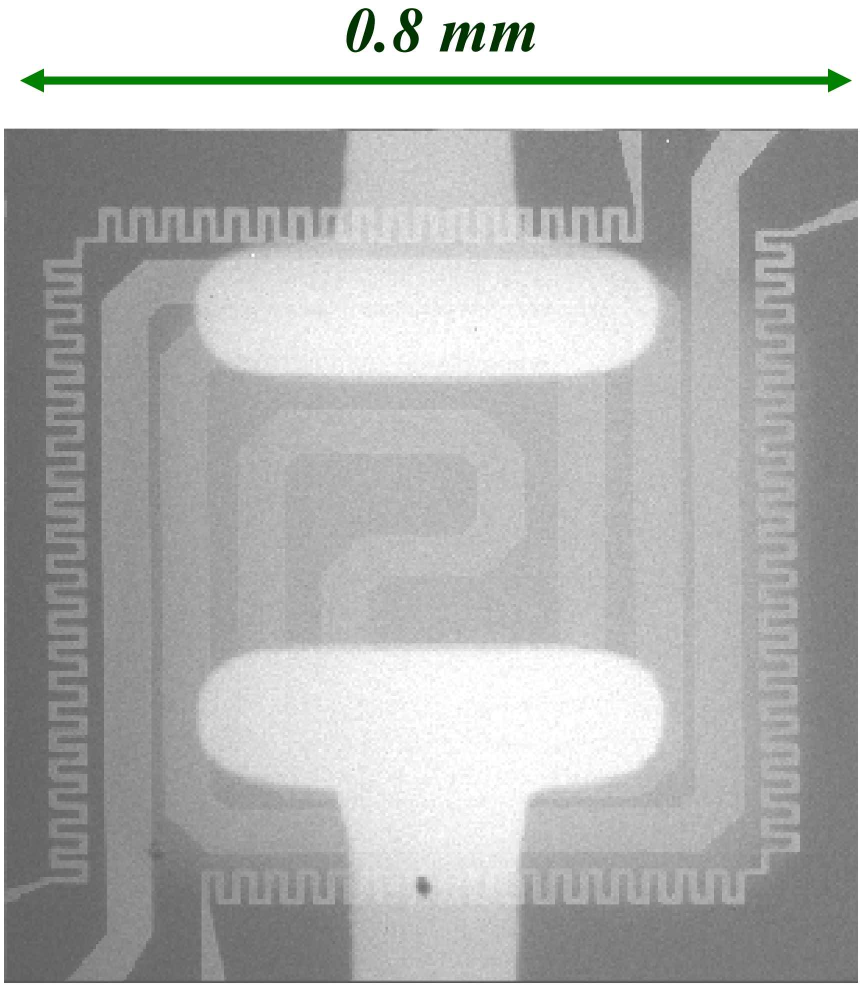
Deposition of SnO_2 and contact pads

12 lead TO-8 package



Sensor packaging

SEM IMAGE OF SENSOR DEVICE SHOWING Si_3N_4 MEMBRANE

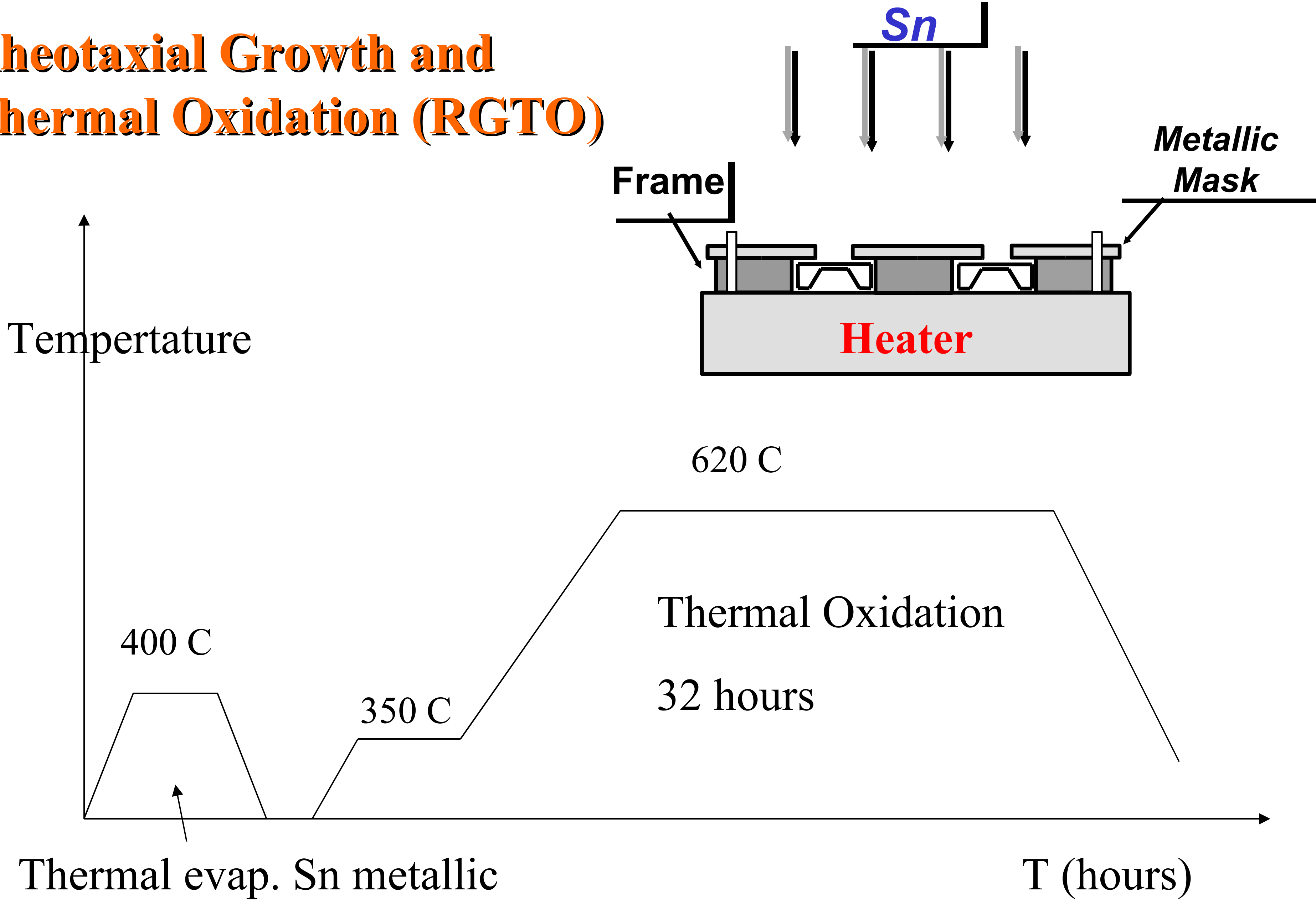


Methods for SnO_2 thin film deposition on nitride membrane

evaporation + thermal evaporation (RTGO)

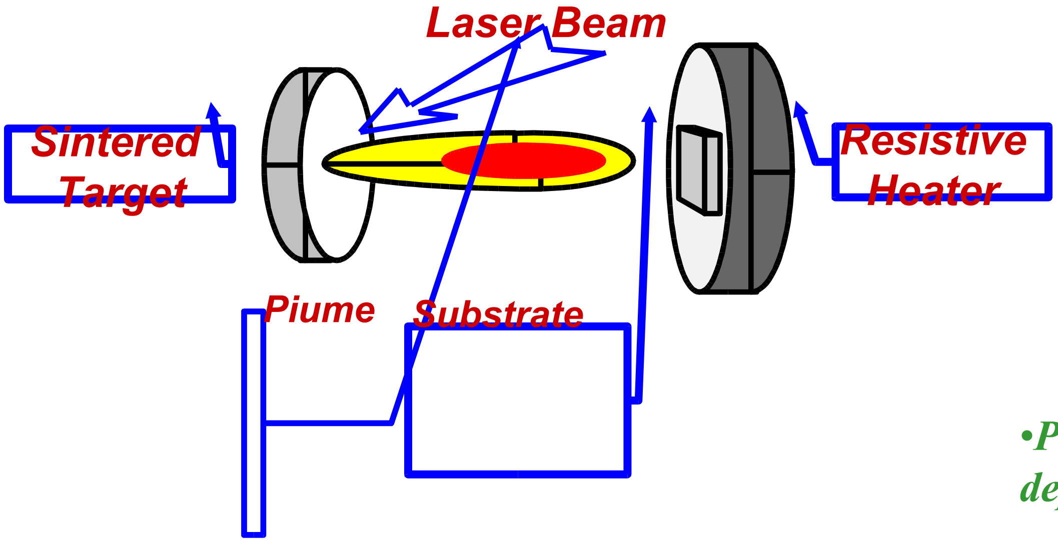
pulsed laser depositon (PLD)

Rheotaxial Growth and Thermal Oxidation (RGTO)



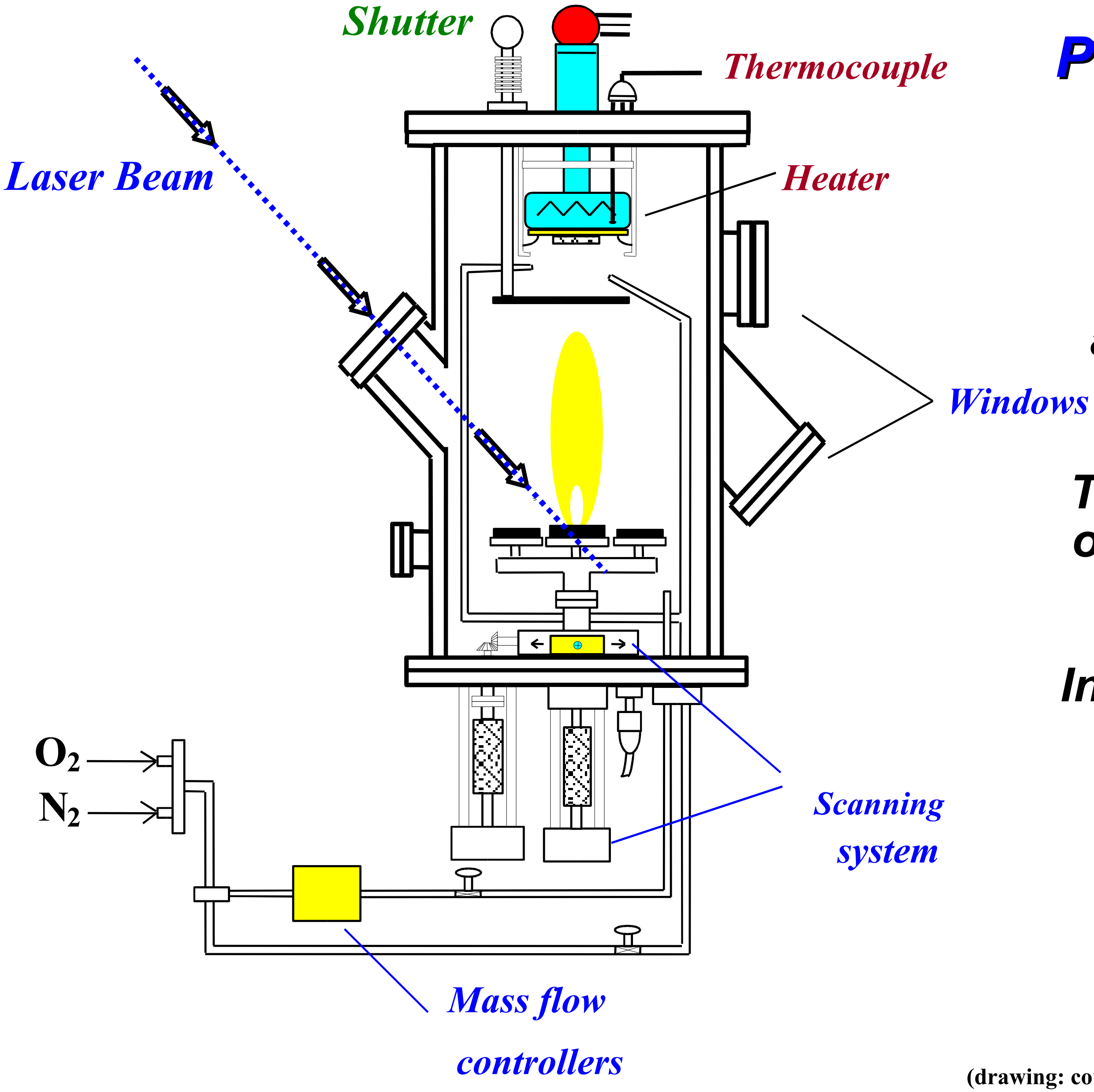
.Demare, R.Sanjines, *Gas Sensor,* Ed. by Sberveglieri, Kluwer Acad. Publ., Netherlands,1992.

Pulsed Laser Ablation Deposition Scheme



- *PLD is a flexible technique for thin film deposition*
- *A wide range on evaporation conditions could be used (laser fluence, gas pressure, reactive environments, ...)*
- *Different materials and various thin films could be deposited with multitarget system;*
- *In situ oxidation*

Pulsed Laser Ablation Deposition System



Deposition Chamber and Energy Source are completely decoupled

This allows a wide range of deposition conditions (Laser Fluence, Gas Pressure, Reactive or Inert environments, …….)

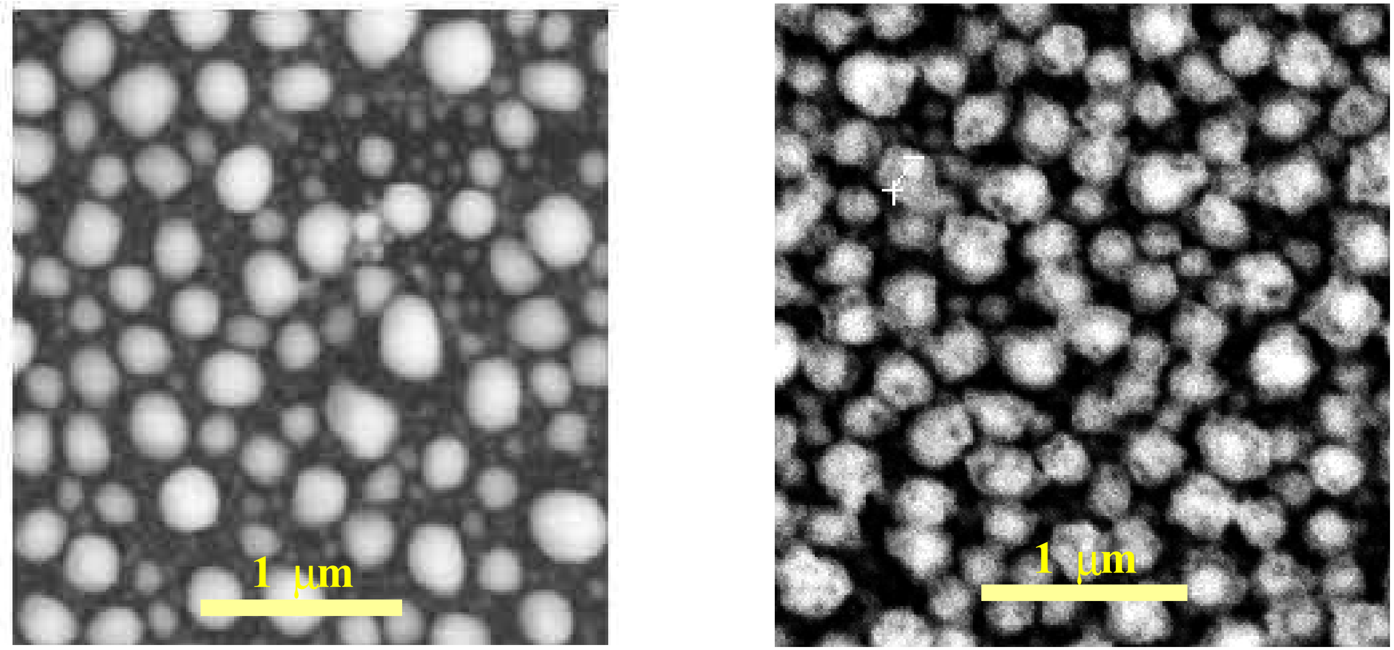
MultiTarget facility available

(drawing: courtesy of S. Nicoletti , IMM-CNR Bologna Italy)

Structural Charaterization of the SnO_2 thin films

Thin Film before and after thermal oxidation

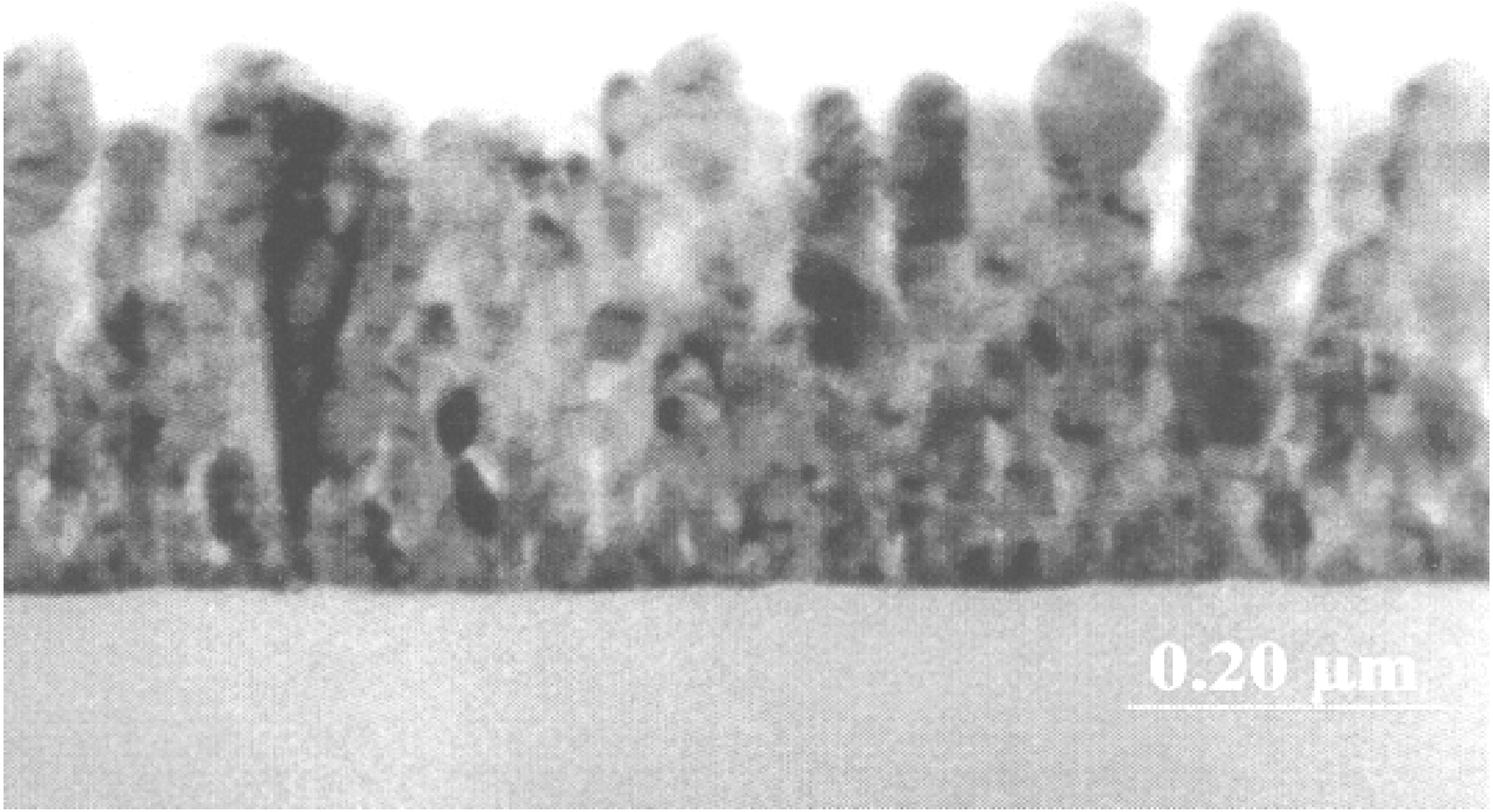
Rheotaxial Growth and Thermal Oxidation (RGTO)



Left: SEM micrograph showing metallic drops of Sn before thermal oxidation.
Right: SEM micrograph showing SnO_2 grains after oxidation

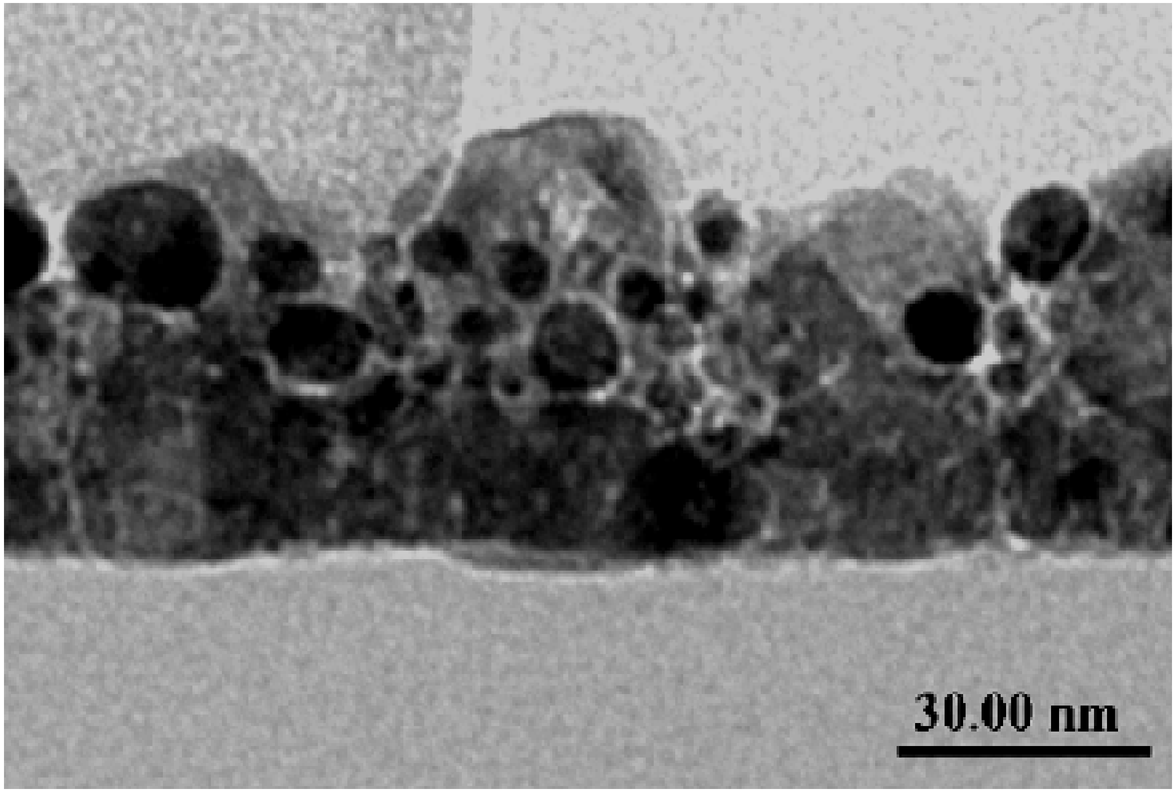
30 nm + 1200 nm steps better relation Surface/volume

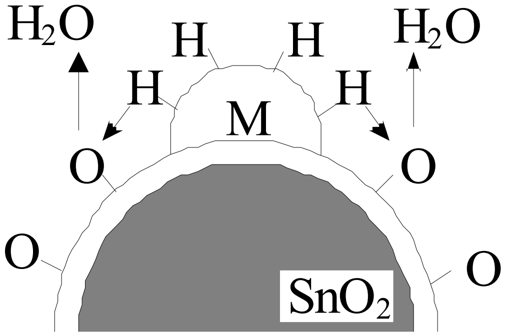
TEM Micrograph of the SnO_2 film



TEM micrograph showing grains with high porosity and high specific surface

Doping of SnO2 thin film surface using catalysts





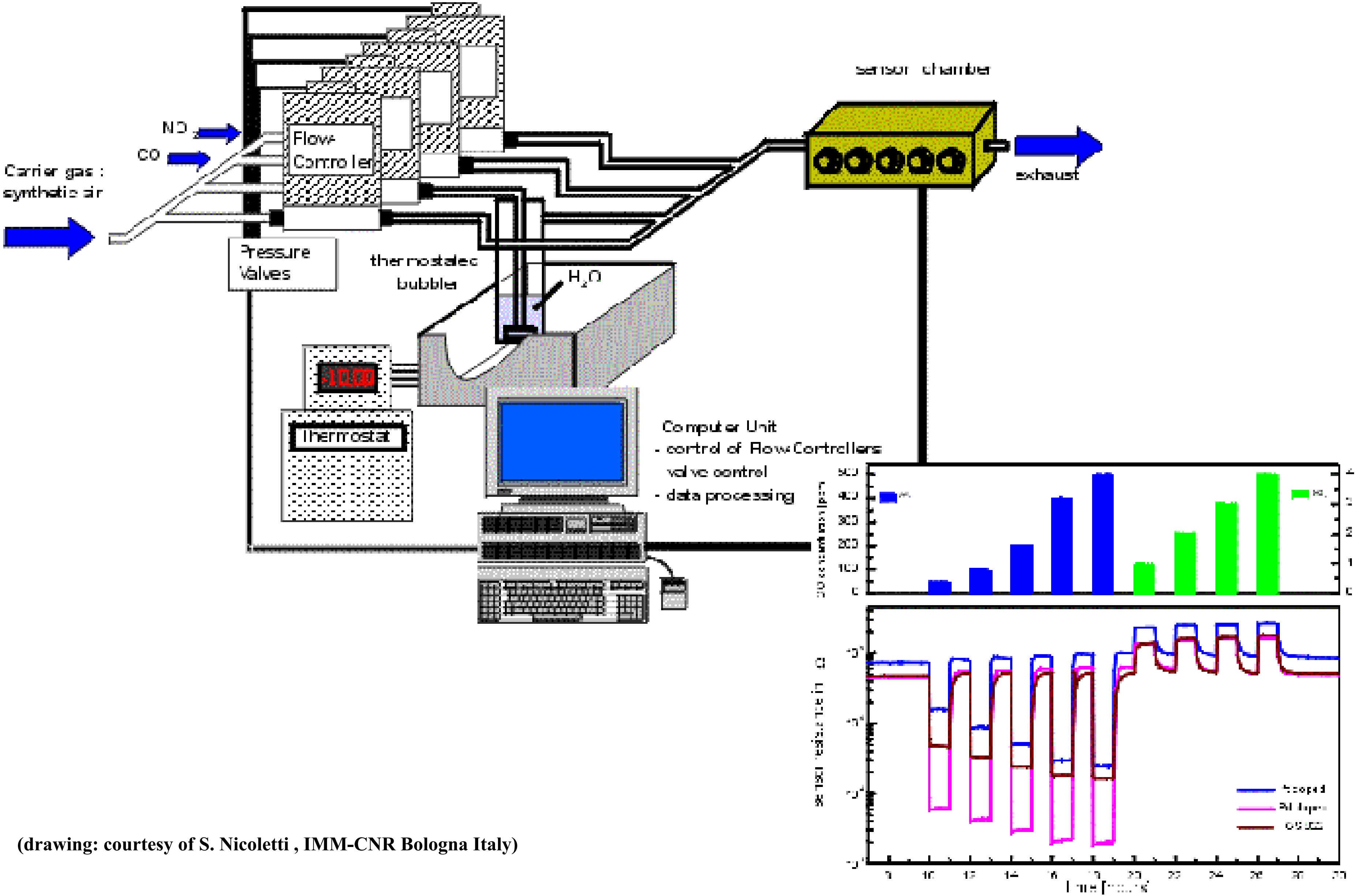
Spillover

TEM micrograph showing doping material nano-drops for enhacing selectivity to certain gas species

Full oxidation of the SnO_2 thin film

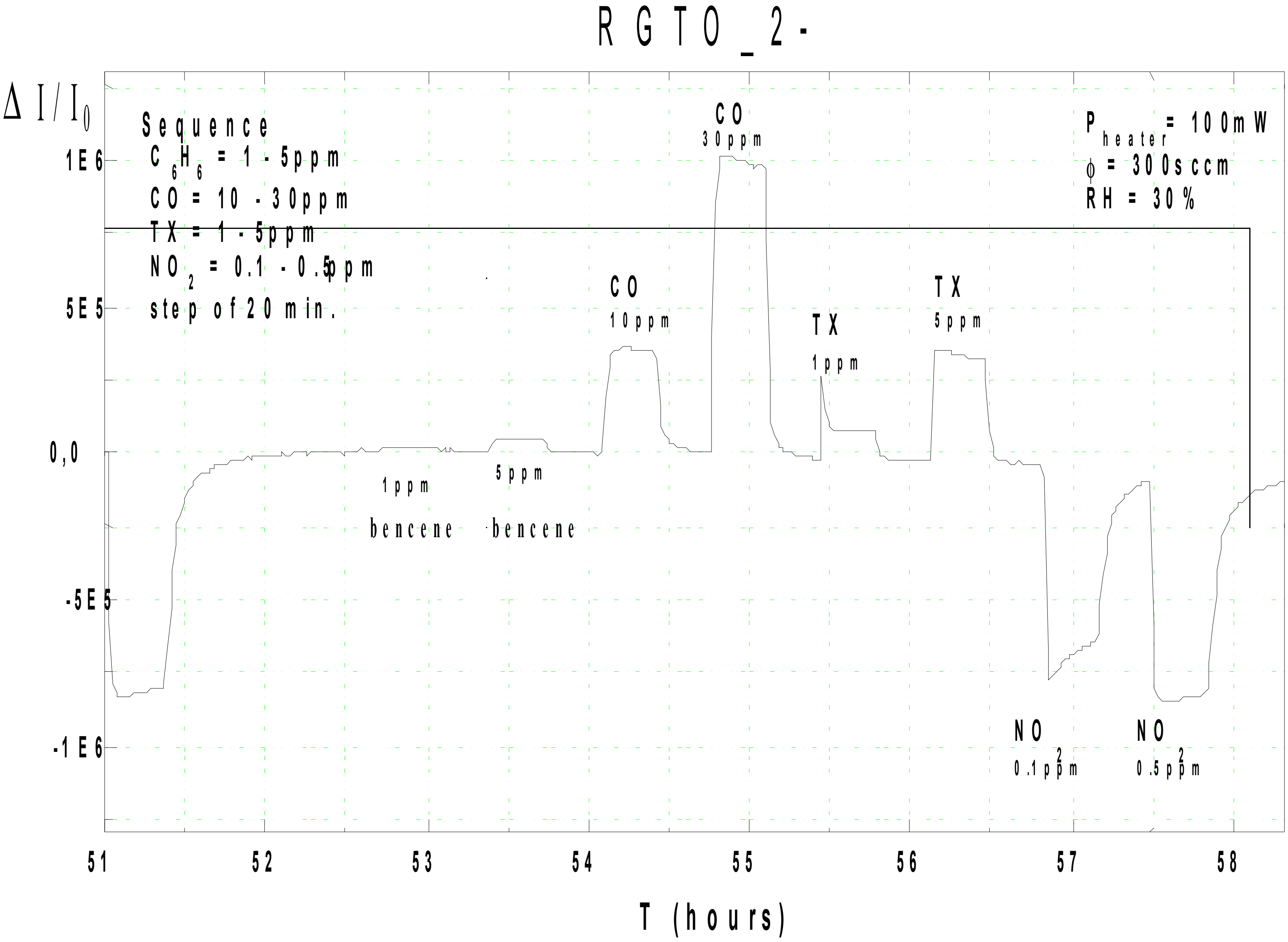
Functional Charaterization of sensors

gas mixer/chamber with humidity control system for quantitative sensor characterization



(drawing: courtesy of S. Nicoletti , IMM-CNR Bologna Italy)

gas mixer/chamber with humidity control system for quantitative sensor characterization



Functional characterization of an undoped SnO$_2$ sensor

Why MEMS gas sensors ?

- ***IC compatible fabrication process***
- ***Low thermal conductivity of the Si_3N_4/SiO_2 membrane => low power consumption***
- ***Thin film => Reduced thermal device mass = > Rise Time and Recover Time ≅ 30 ms***

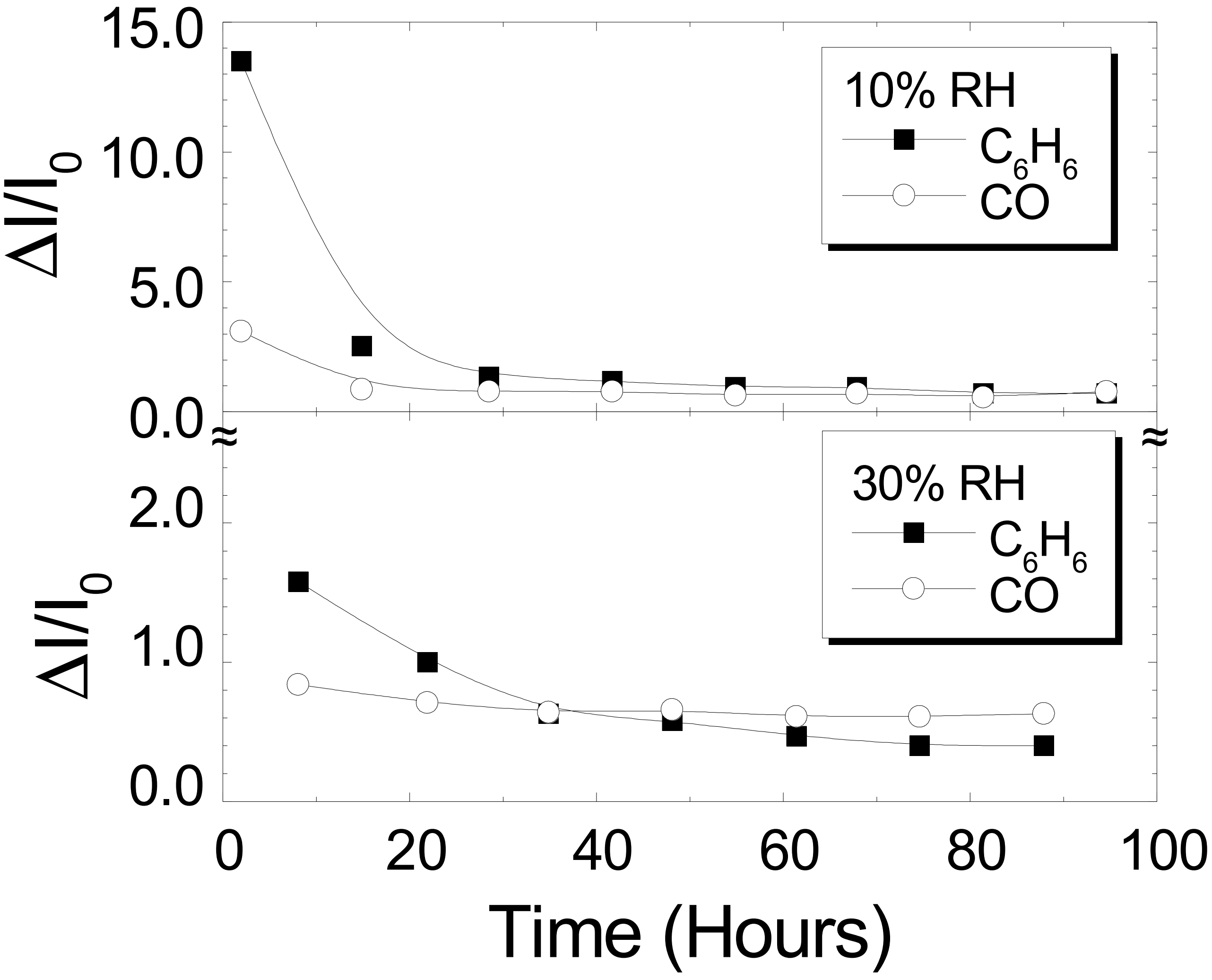
- ***HAND HELD DEVICES !***

Problems to be solved

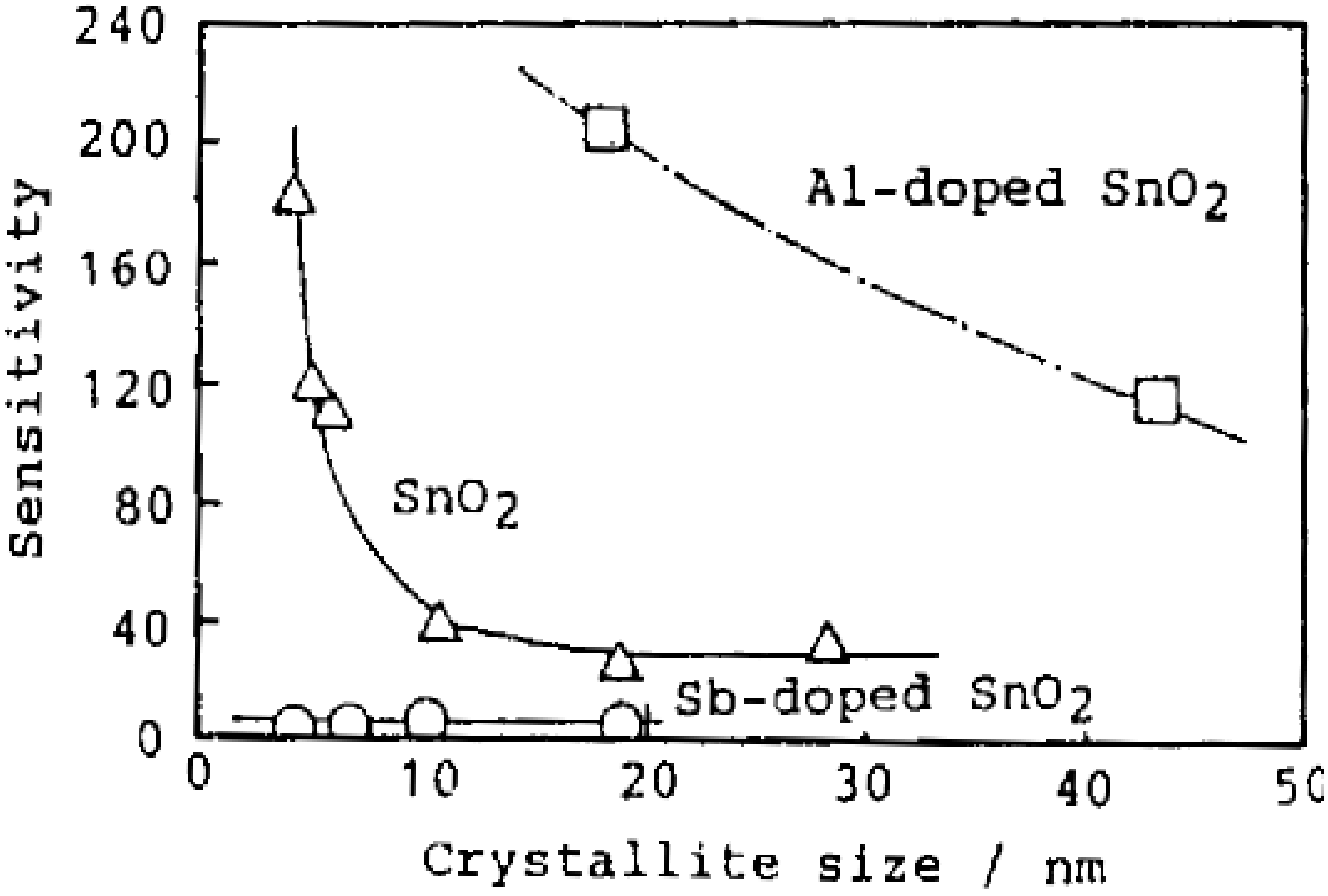
The loose of sensibility with time , the so called “aging” of the sensor

All technologies of gas sensors has this problem

$\Delta I/I_0$ as a function of the ageing time



Effects of grain size and geometry of grain connections (SnO_2)



Sensitivity is highly dependent on grain size

Applications

gas monitor

electronic noses

SMOG

Smart air pollution **M**onit**O**rin**G** networks

Research project funded by the European Commission under the ESPRIT programme

The monitoring unit is based on an array of solid-state sensors achieved by using innovative materials and technologies for measuring **Carbon monoxide, Nitrogen dioxide, Ozone, Benzene.**

Analytical limits of the pollutants monitored[1]

Pollutant	Minimum detectable level	Pre-alarm limit	Alarm limit
Carbon Monoxide CO	1	13	26
Nitrogen Dioxide NO_2	0.05	0.1	0.2
Ozone O_3	0.01	0.1	0.2
Benzene C_6H_6	0.5[2]	0.05	0.01

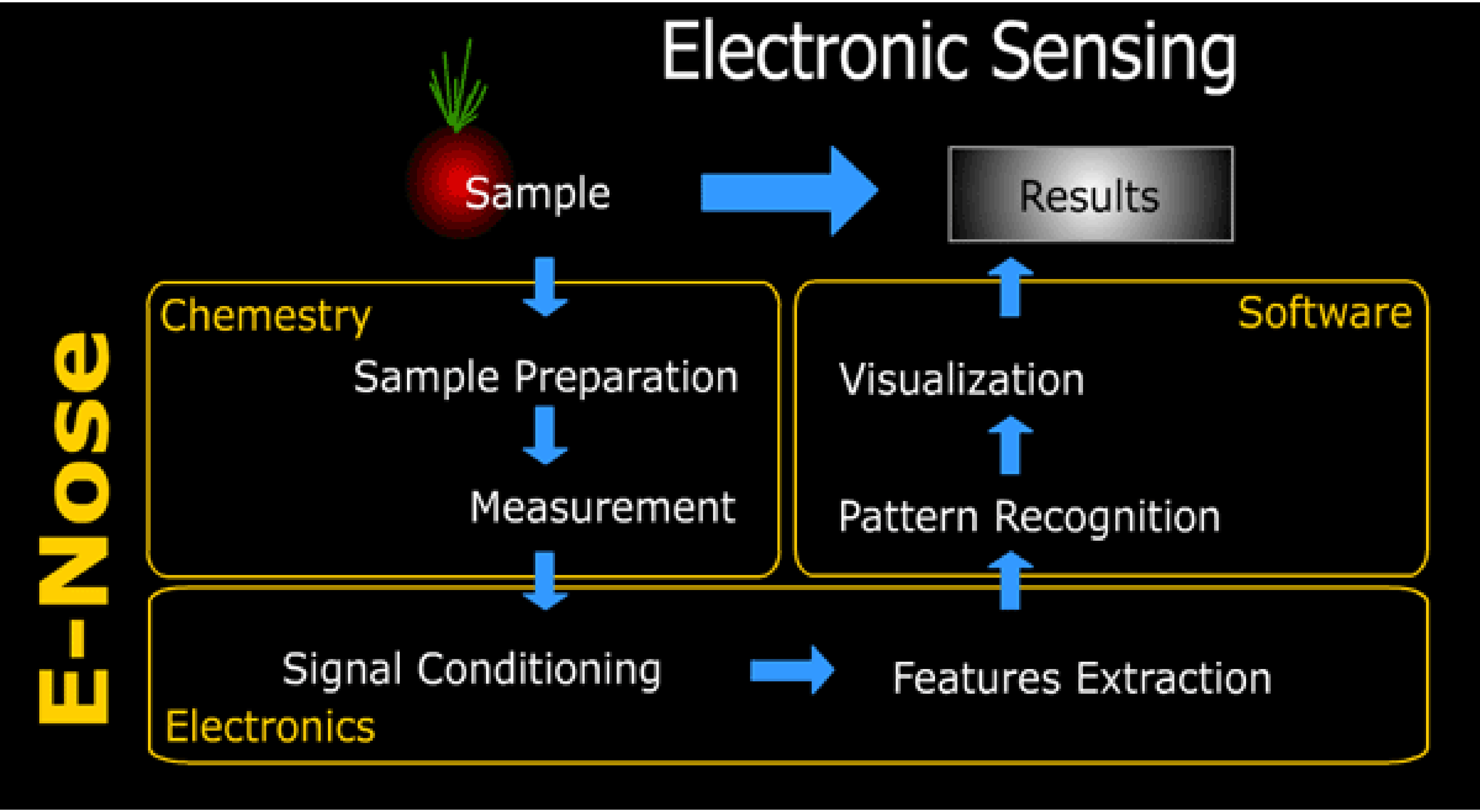
[1] Values indicated in ppm

[2] A pre-concentrator is used to increase sensor sensitivity

Features

- small size for enhanced compatibility with a multitude of applications;
- power saving;
- elements made on substrata of microprocessed Si in order to obtain miniaturized thin-film sensors with low power consumption rates at the maximum running temperatures of the sensors themselves;
- solid-state sensors made with technologies compatible with the typical production processes of integrated circuit technologies; such sensors feature excellent stability in time and excellent reproducibility of the characteristic response to the pollutants of interest;
- miniaturized gas chromatograph for measuring BTX
- development of a miniaturized air sampling system using a pneumatic board, microvalves and micropumps;
- the ability to identify and measure the concentration of the pollutant to be monitored taking into account the deviation in time typical of these sensors by means of pattern recognition techniques (neural networks, fuzzy logic);
- easy to exchange components (sensor units, primary electronics);

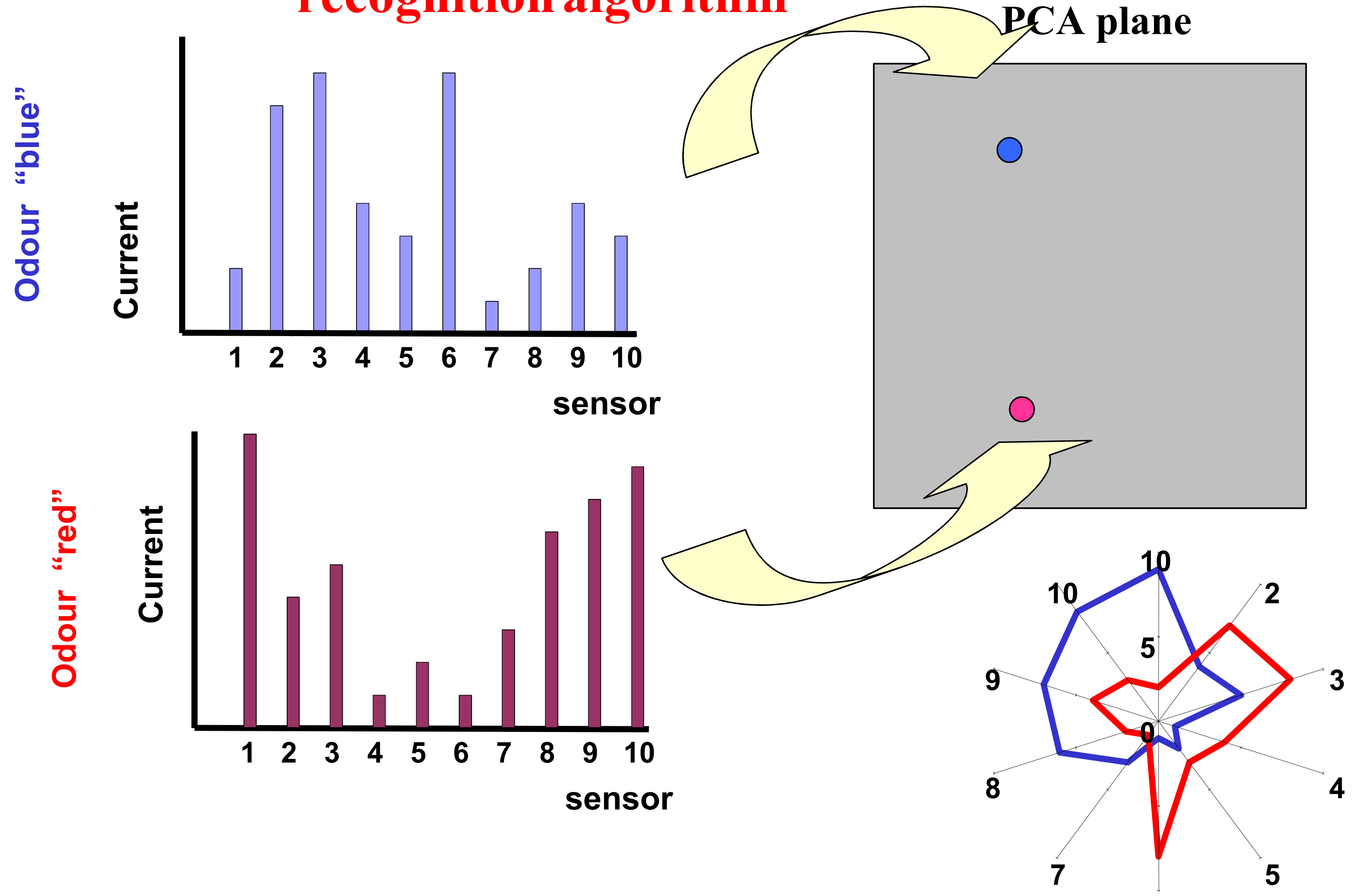
Measurement sequence with e-noses



more information : www.e-nose.com.ar

Electronic nose ≠ gas monitor

recognition algorithm

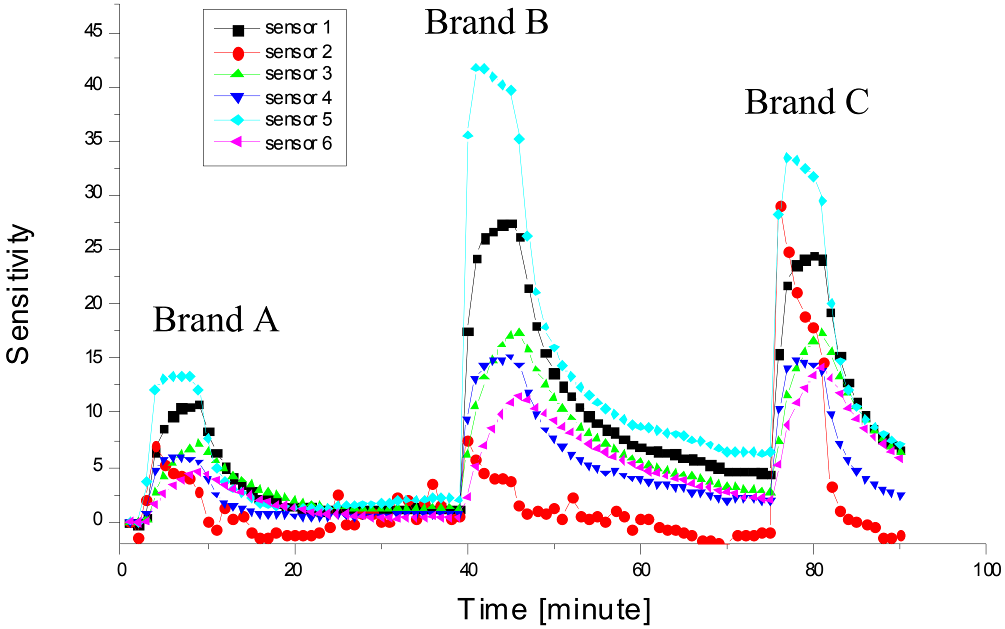


Polar representation = "odour fingerprint"

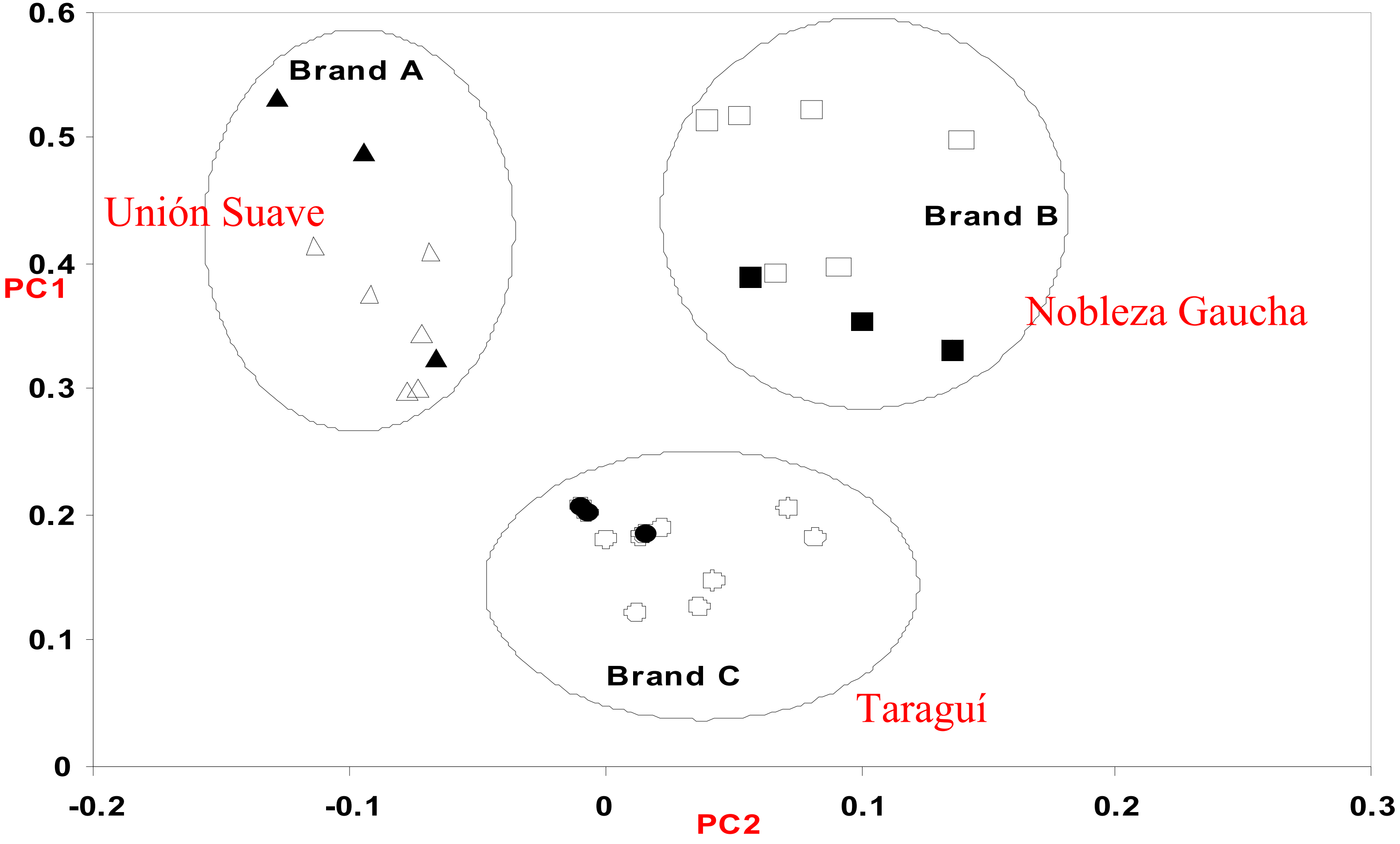
Caracterization of different mate brands

- For each sample, six cyclic exposures to the odour molecules were repeated.
- Each exposure to the mate odour was taken during 3 minutes preceded and followed by an air purge for 20 minutes.
- We analyzed the sensitivity defined as: $S = (I - I_{base})/I_{base}$

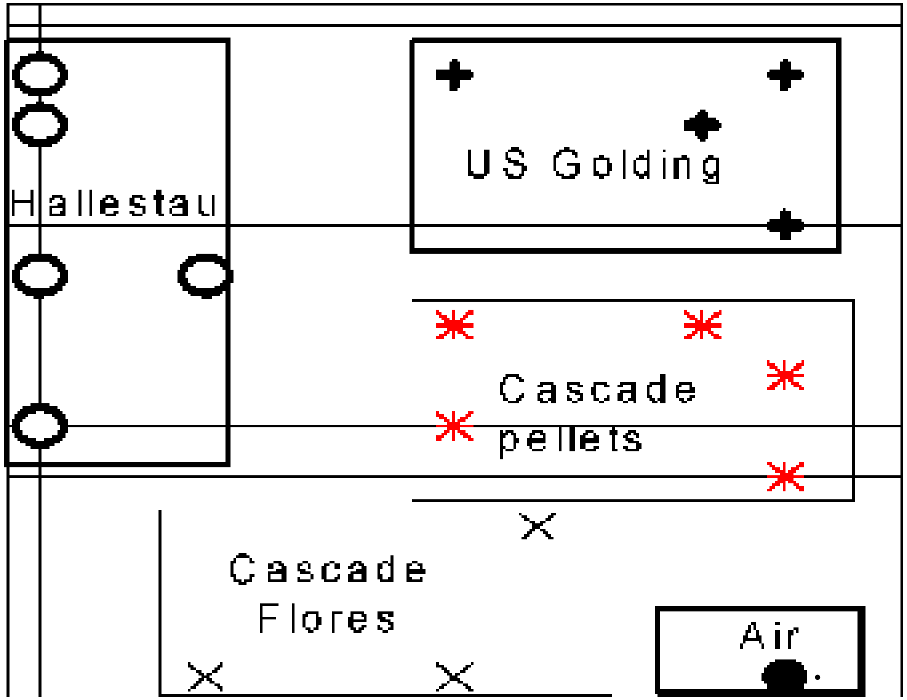
with I (I_{base}) the sensor current in the presence of odour (air).



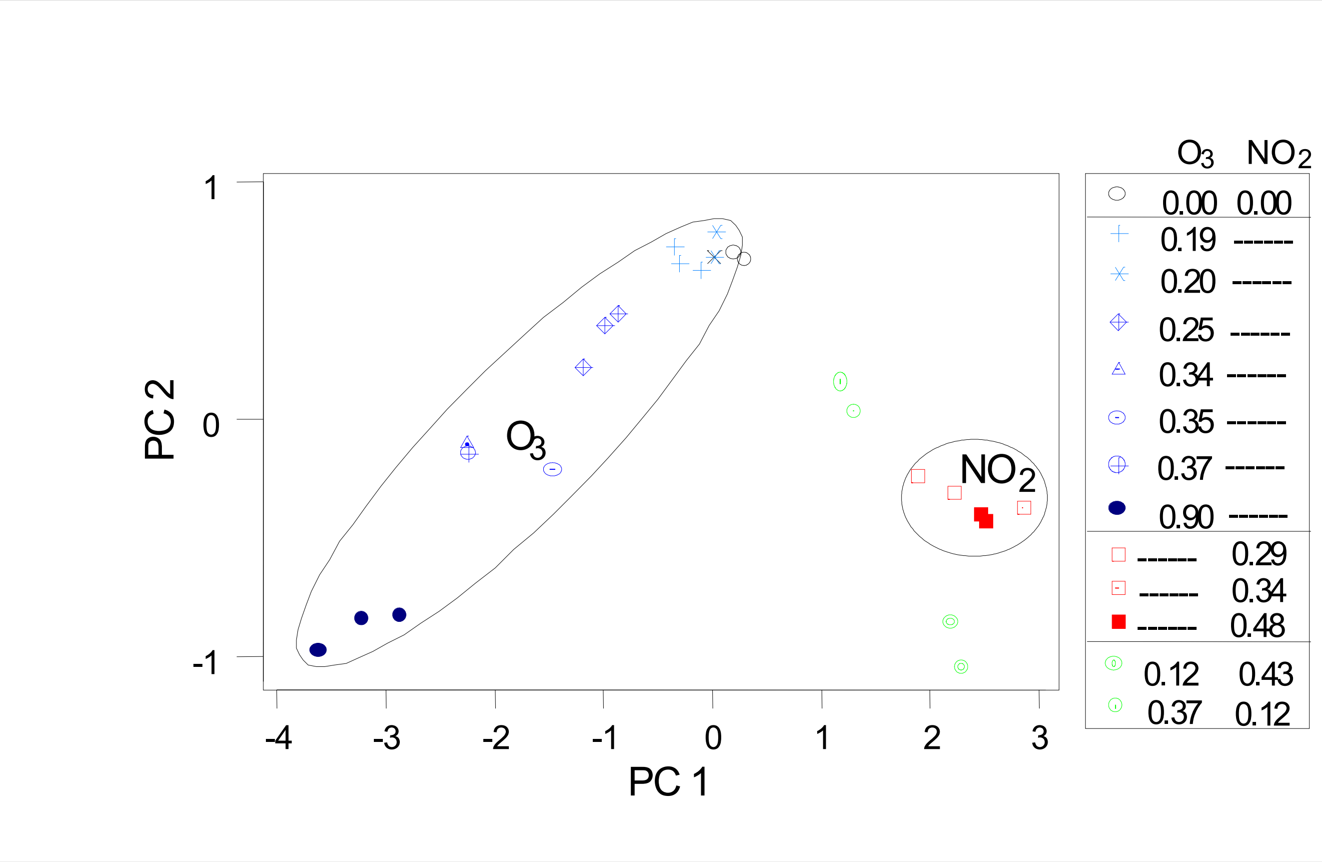
Principal component analysis (PCA) was applied (3). The PCA coefficients were defined using as learning set 18 measurements, 6 for each brand (black points). "Unknown" samples were measured and the corresponding nose response was projected onto the previously defined subspace (red points). The adequacy of the scheme for recognition purposes is evident from the graph.



Self Organizing Maps (SOM) of different samples of hops



Both ozone (O_3) and nitrogen dioxide (NO_2) simultaneously present

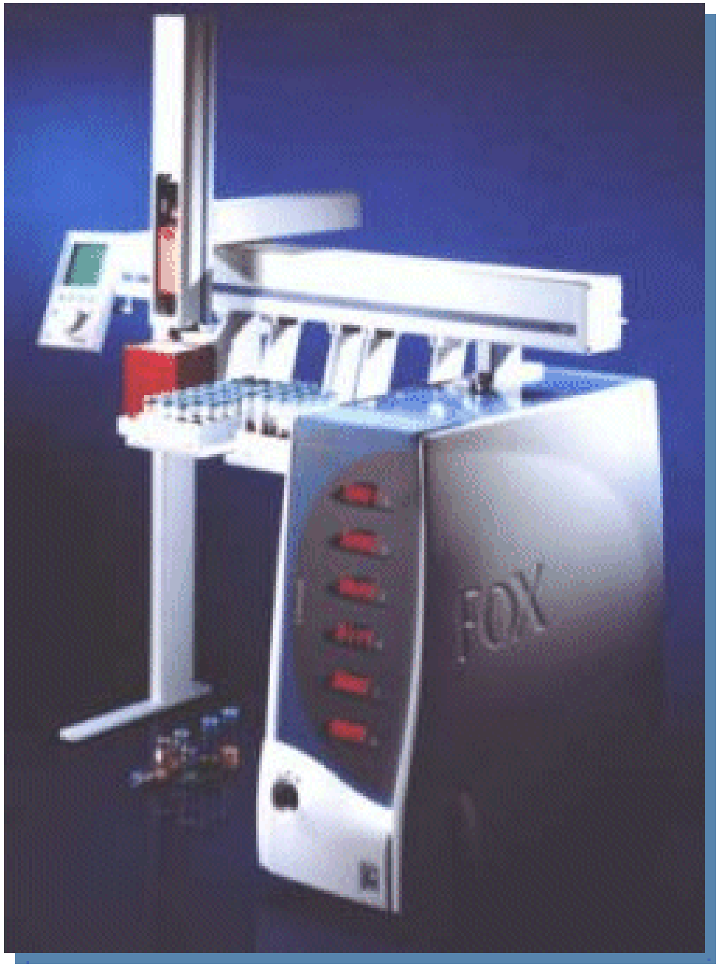


Principal components analysis of ozone and NO_2

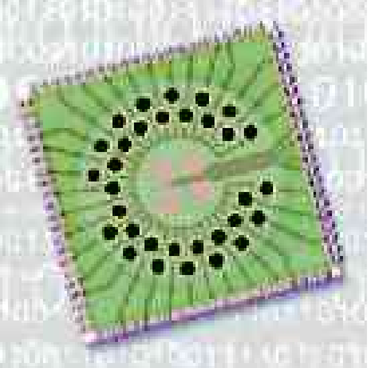
- The presence of either O_3 or NO_2 are clearly discriminated
- The nose response is ambiguous if only a PCA analysis is done, when both oxidants are present with similar concentrations.
- This result is shared by most types of sensor including electrochemical cells.

Commercial Desktop E- NOSE

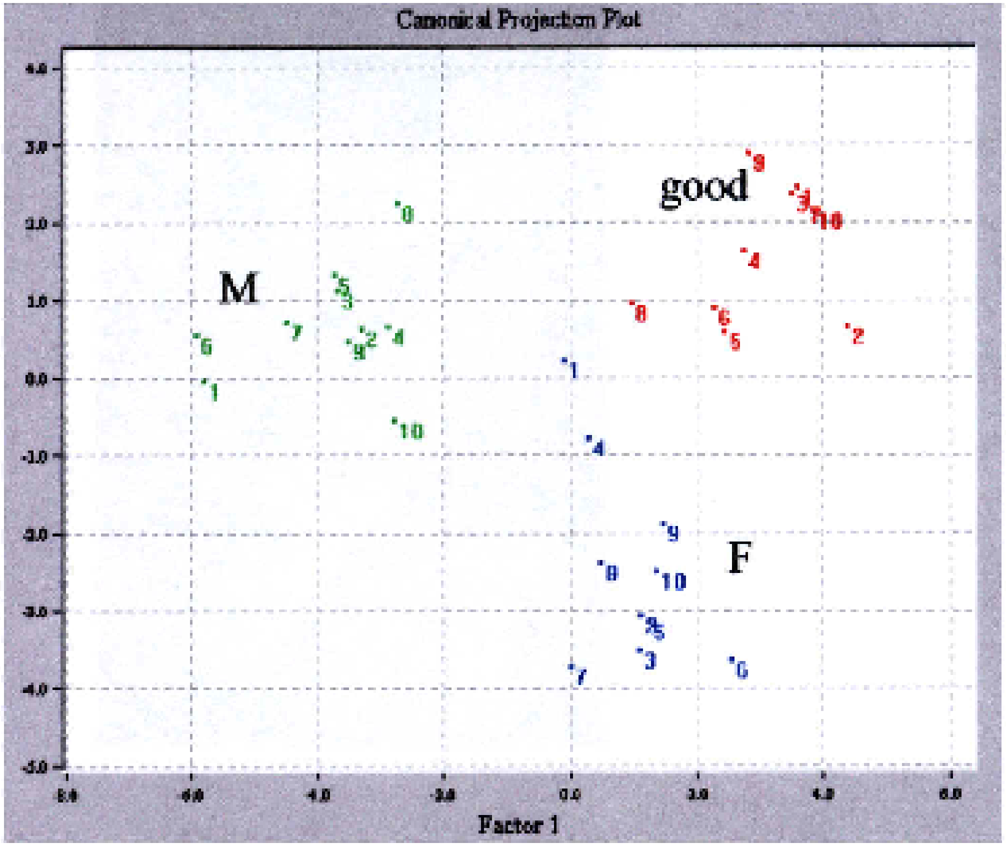
Alpha M.O.S



CYRANO sciences



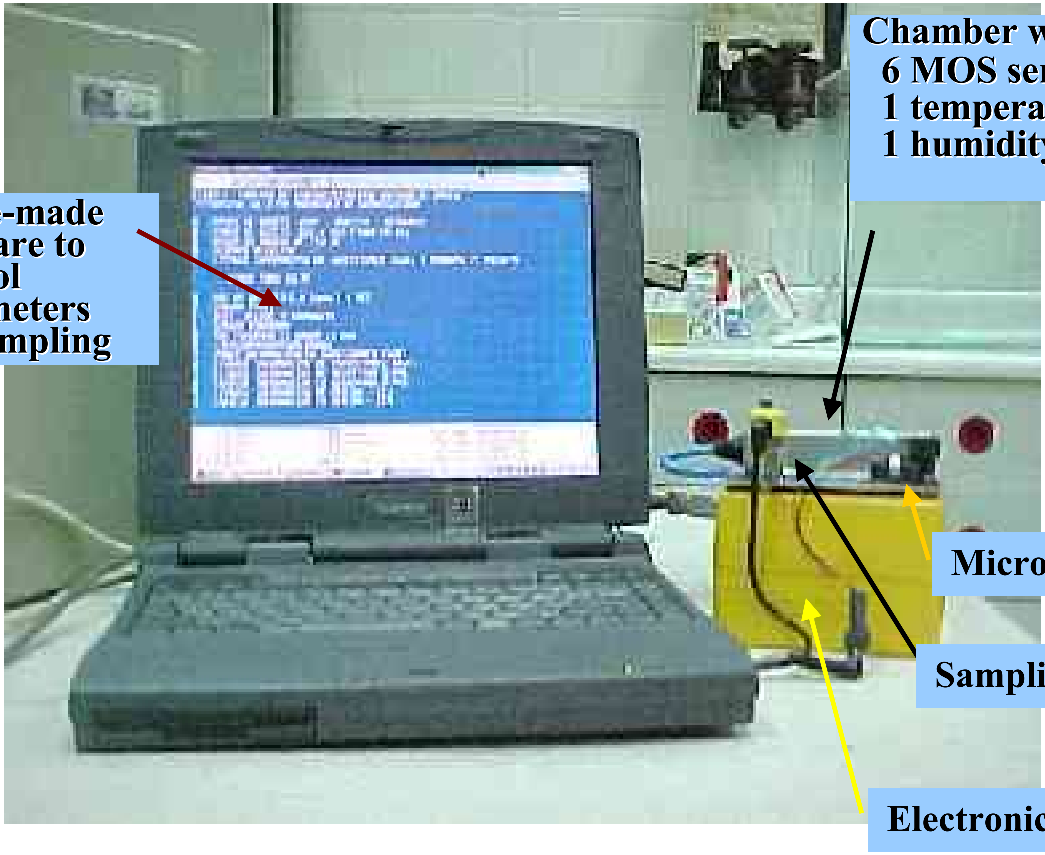
Coomercial Handheld e-nose



Commercial e-noses

AppliedSensor

Our First "Lab Prototype" of Electronic Nose



Home-made software to control parameters for sampling

Chamber with
6 MOS sensors
1 temperature sensor
1 humidity sensor

Micro-Pump

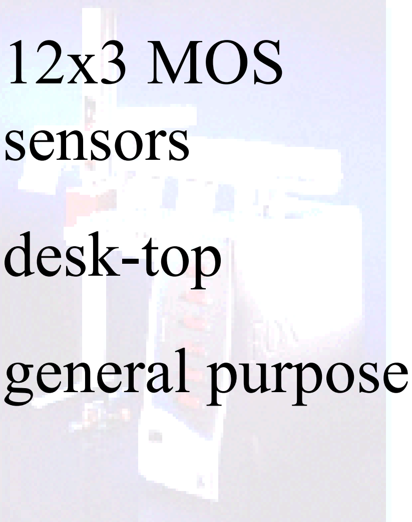
Sampling valve

Electronics

e-nose prototype with array of 6 MOS sensors for air quality control applications

Our development of e-noses under the PID131-2001 contract SECYT-JPA SA

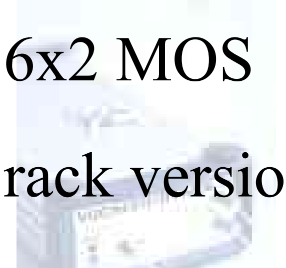
Second “Lab Prototype”
of Electronic Nose (dic-2003)



12x3 MOS sensors

desk-top

general purpose



6x2 MOS

rack version

one /few product

2 versions of “Pre-competitive Prototype”
to be transfered the industry JPA SA
Nov. 2004

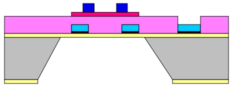
Market prospective

Product Types	1996 Units (millions)	$ (millions)	2002 Units (millions)	$ (millions)
Drug delivery systems	1	10	100	1000
Optical switches	1	50	40	1000
Lab on ship	0	0	100	1000
Magneto optical heads	0.01	1	100	500
Projection valves	0.1	10	1	300
Coil on chip	20	10	600	100
Micro relays	0.1	50	100	
Micro motors	0.1	5	2	80
Inclinometers	1	10	20	70
Injection nozzles	10	10	30	30
Anti-collision sensors	0.01	0.5	2	20
Electronic noses	0.001	0.1	0.05	5
TOTAL	33	$107	1045	$4,205

Table 4. Worldwide M 3 market size in 1996 and 2002 foremerging MEMS product types in $US millions (Prime Faraday Partnership ,Wolfson School of Mech. And Manuf. Eng., Loughborough University, UK, 2002)

E-nose group challenges and future trends

Single MOS sensor per membrane



CNEA-Citefa

Multiple MOS sensor per membrane (single nose chip sensor). Two concepts in “draft” to be implemented (2005-2006)

Conventional Electronics

CeTAD -Citefa

IC custom made (2006)

PME 109

¿ JPA SA? +...R&D groups

Hand held e-nose few odours but reliable (2007)

Summary

* Develop a MEMS gas sensor and an application , e-nose, with the National Agency of Science and Tech funds and an industrial partner (www.e-nose.com.ar)

* Start-up with a MEMS activity at CNEA and a cooperation with other R&D Institutes that allows us to develop more interesting devices

* We received funds for modernizing the lab equipment that will allow us test new gas sensors devices for a new generation of handheld e-noses