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

COST Action TD1105

WGs & MC Meeting at SOFIA (BG), 16-18 December 2015

New Sensing Technologies for Indoor Air Quality Monitoring: Trends and Challenges

Action Start date: 01/07/2012 - Action End date: 30/04/2016 - Year 4: 1 July 2015 - 30 April 2016

Highly Sensitive and Durable Ozone Sensing Elements

CRETE CENTER FOR QUANTUM COMPLEXITY AND NANOTECHNOLOGY

FORTH Foundation for Research & Technology - Hellas

Dr. Vassilios Binas

Function in the Action WG1 Member

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cost EUROPEAN COOPERATION IN SCIENCE AND TECHNOLOGY

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

COST is supported by the EU Framework Programme

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FORTH consists of 7 Research Institutes located throughout Greece
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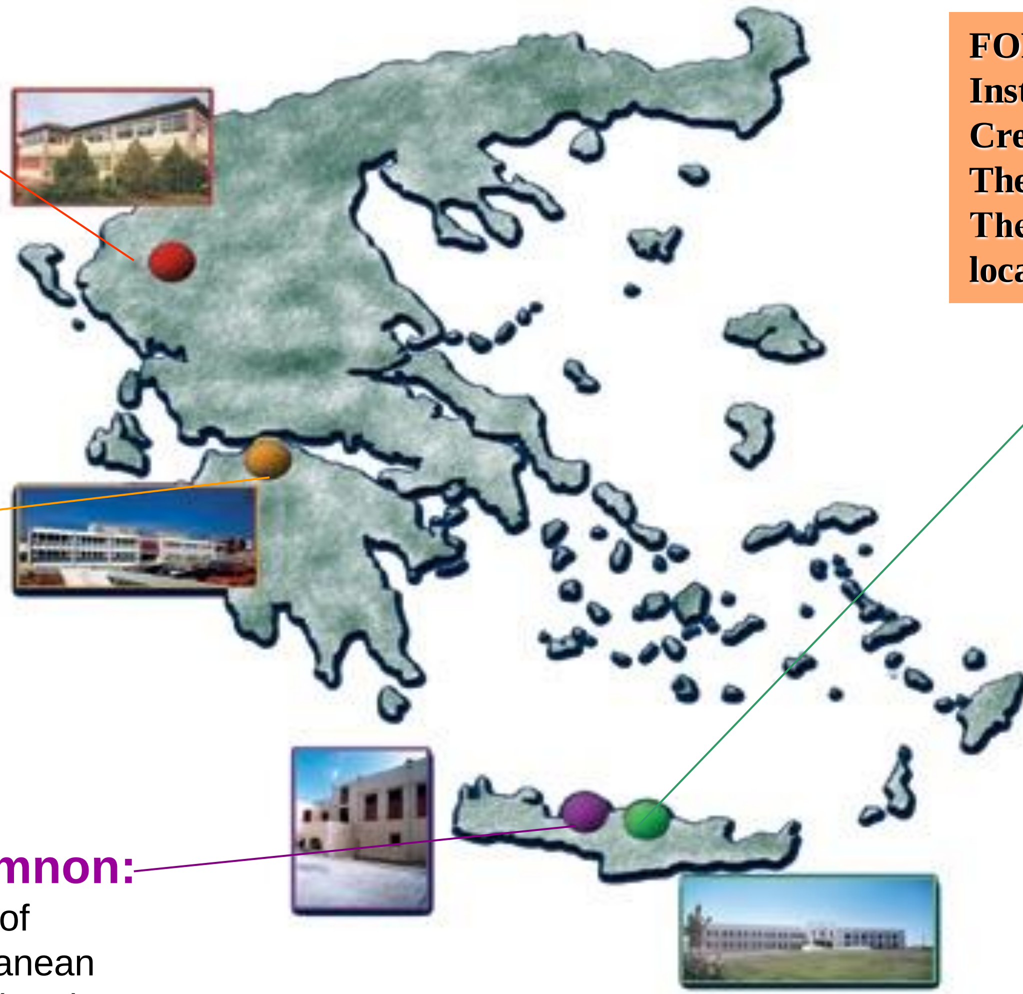
The Foundation's headquarters are located in Heraklion, Crete



Ioannina:

Biomedical Research Institute (**BRI**)

Patra:

Institute of Chemical Engineering and High Temperature Chemical Processes (ICE-HT)

Rethymnon:

Institute of Metiderranean Studies (**IMS**)

Heraklion HQ:

- **Institute of Electronic Structure and laser (IESL)**
- **Institute of Molecular Biology and Biotechnology (IMBB)**
- **Institute of Computer Science (ICS)**
- **Institute of Applied and Computational Mathematics (IACM)**

Crete Center for Quantum Complexity and Nanotechnology

Department of Physics, University of Crete

REGPOT Program

1 September 2013 – 28 February 2017
9 Partner Institution
Over 30 postdoctoral associates and senior associates

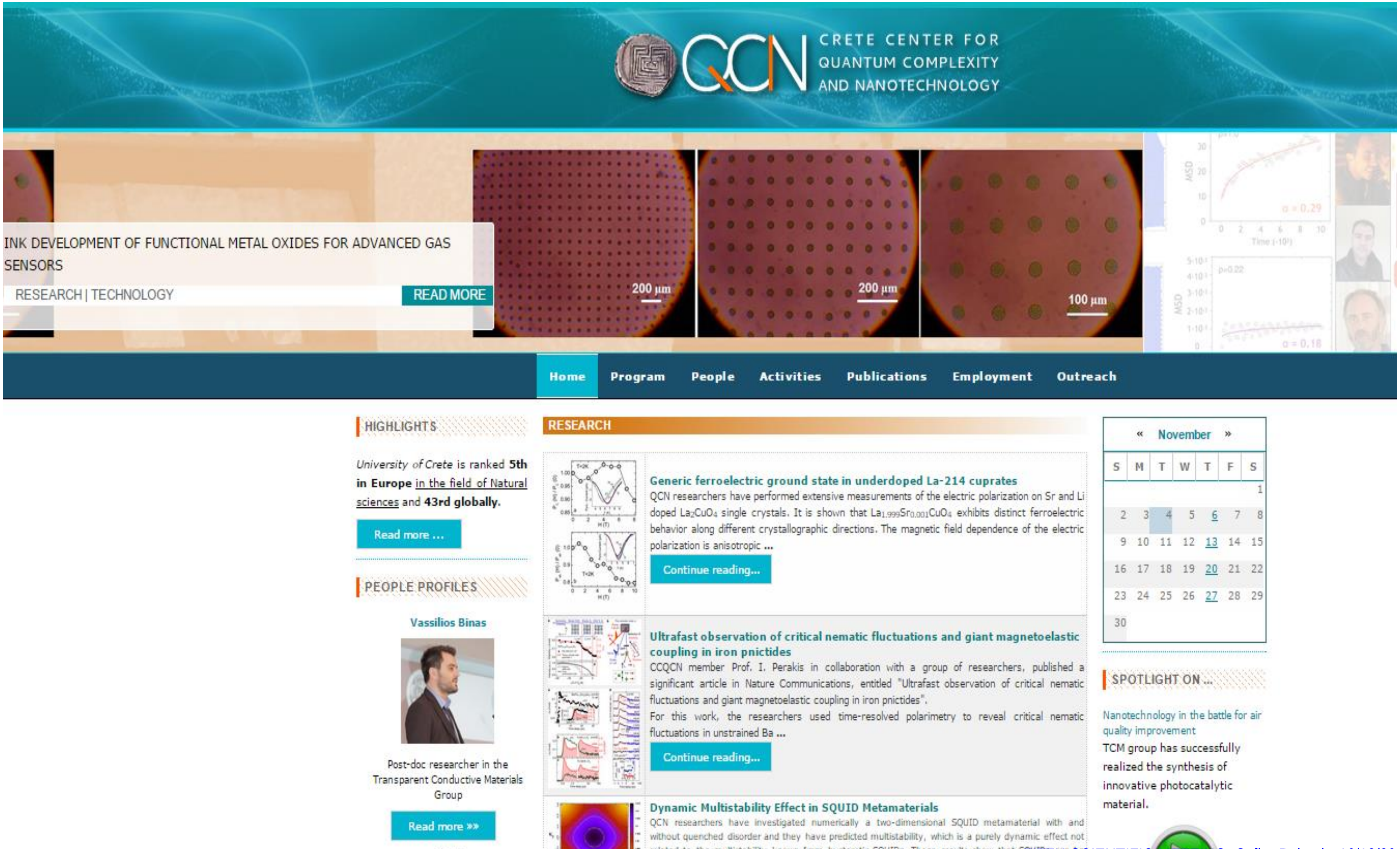
qcn.physics.uoc.gr

The aim:

- Create a High performance Nanotechnology Center
- Form of a local CENTER OF EXCELENCE in Theoretical, Computational and Experimental Physics, Chemistry and Materials Science with long term viability
- Connect with the local economy and induce smart specialization

Crete Center for Quantum Complexity and Nanotechnology

Department of Physics, University of Crete

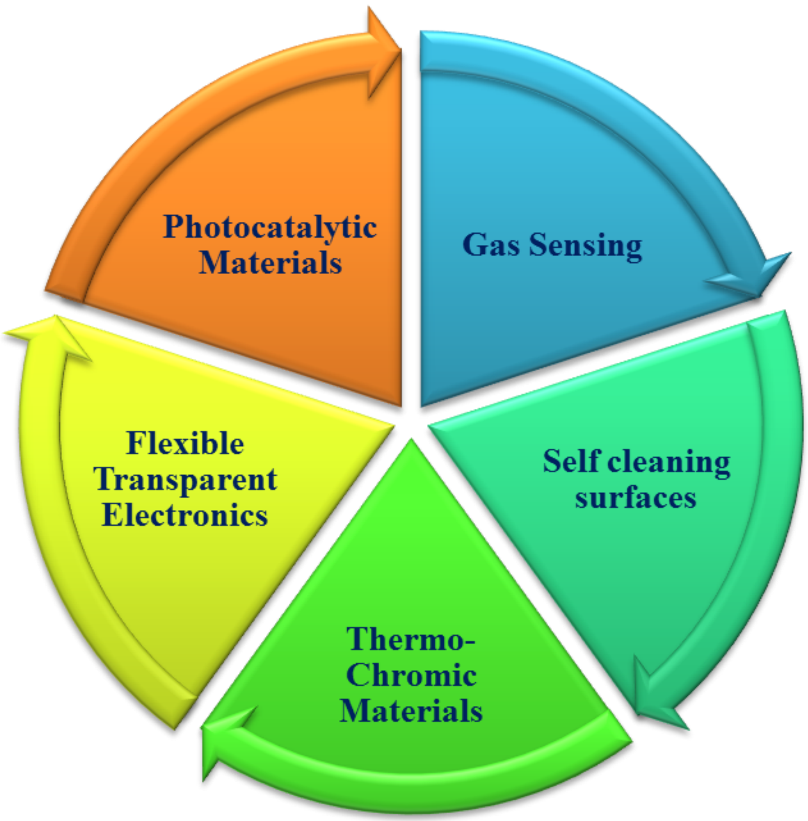


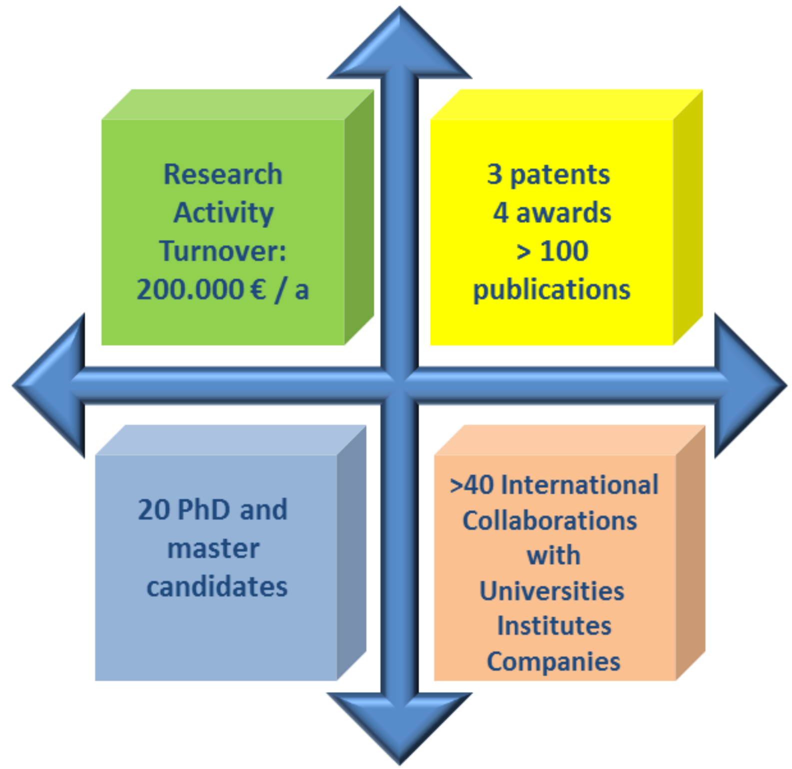
Transparent Conductive Materials Group

What we do

Transition Metal Oxides

Powder	Sols (Inks)	Thin films





- **Introduction**

  - Chemical sensors (definition, applications etc)

  - Metal Oxides Semiconductors

  - Why Ozone??

- **Our Research activities** on Gas Sensors

- **Highly Sensitive** and **Durable** *Ozone Sensing Elements*

- **Conclusions**

Chemical sensors definition and classification

A **chemical sensor** is a device that *transforms chemical information, ranging from the concentration of a specific sample component to total composition analysis, into an analytically useful signal*. The chemical information, mentioned above, may originate from a chemical reaction of the analyte or from a physical property of the system investigated.

In **solid state** (chemical) **gas sensors** the input signal is the concentration of one or more gaseous species in a carrier (an unknown pattern in Electronic Noses) and the sensor is solid.

Pure & App. Chern., Vol. 63, No. 9, pp. 1247-1250, 1991

Chemical sensors definition and classification

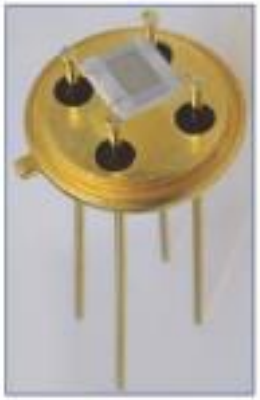
Chemical sensor may be classified according to the operating principle of the tranducer. Optical / Electrochemical / Electrical / Mass Sensitive / Magnetic / Thermometric devices

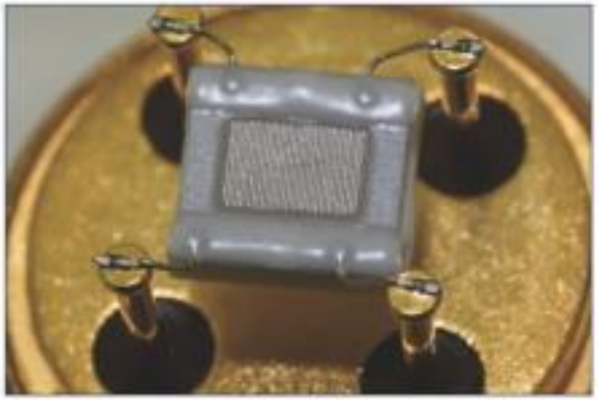
Electrical devices based on measurements, where no electrochemical processes take place, but the signal arises from the change of electrical properties caused by the interaction of the analyte.

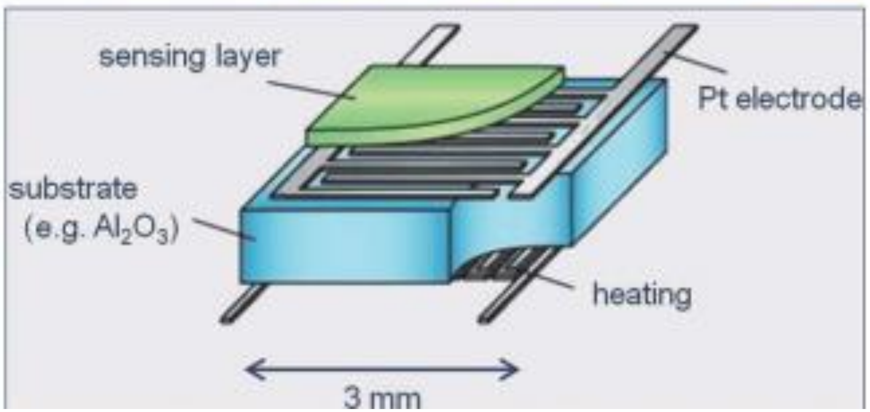
Metal oxide semiconductor sensors used principally as gas phase detectors, based on reversible redox processes of analyte gas components.

Pure & App. Chern., Vol. 63, No. 9, pp. 1247-1250, 1991

Chemical Sensors







- **Sensitivity**
- **Selectivity**
- **Stability**

- **Recovery time**
- **Economic efficiency**

  - low manufacturing costs

  - low operating temperatures

Gas Sensors Applications

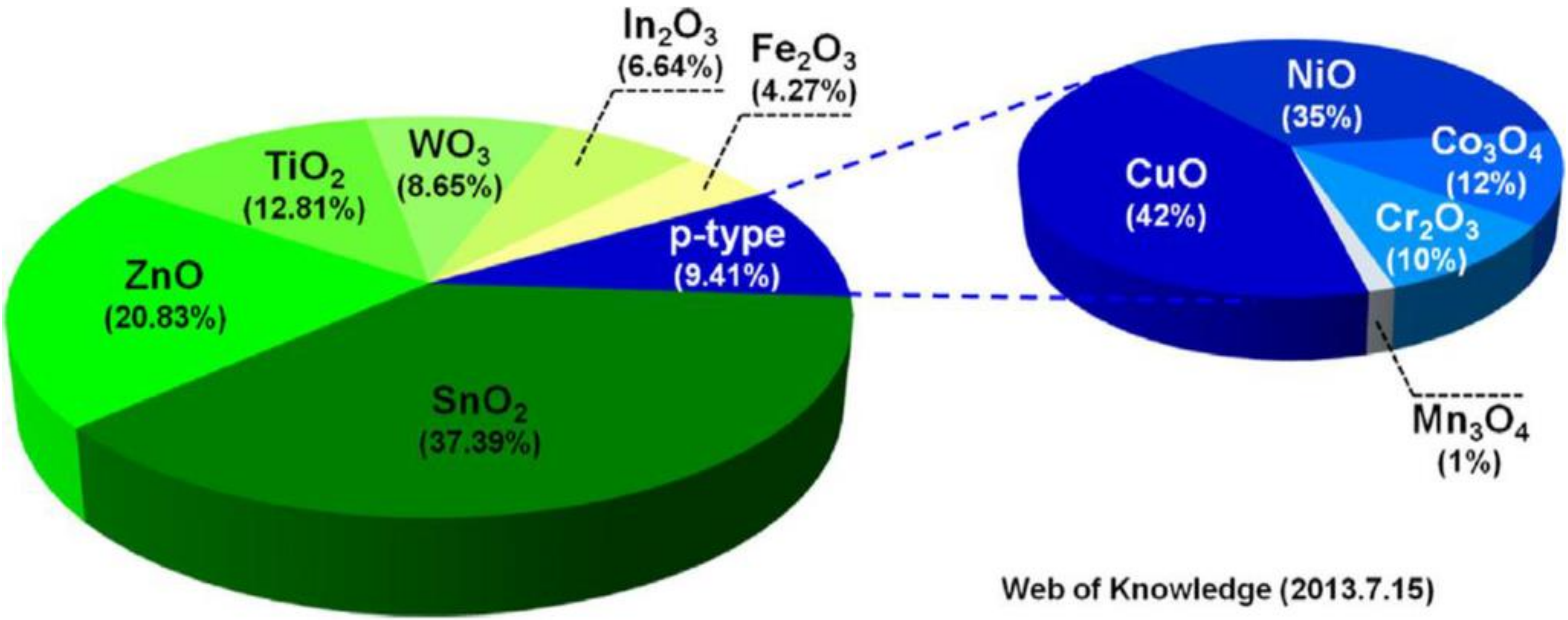
- **Automotive, industrial and aerospace sector** (safety, comfort, combustion control and exhaust gases monitoring)
- **Food industries**
- **Security sector**
- **Environmental monitoring**
- **Medical sector** (diagnosis and parient monitoring)
- **Home** (safety, comfort, etc)

Metal Oxide Conductometric (resistive) gas sensors

- Metal Oxide Semiconductor gas sensors are **high gap ionic semiconductors.** Donors are oxygen vacancies.
- A change of the surrounding environment modifies **electrical transport properties** of Metal Oxide Semiconductors
- Metal Oxide Semiconductors are promising devices **(small dimension, low cost, low power consumption, on-line operation and high compatibility with microelectronic processing)**
- **Application field:** environmental monitoring, automotive applications, air conditioning in airplanes, spacecrafts and houses, sensors networks.

Metal Oxide Conductometric (resistive) gas sensors

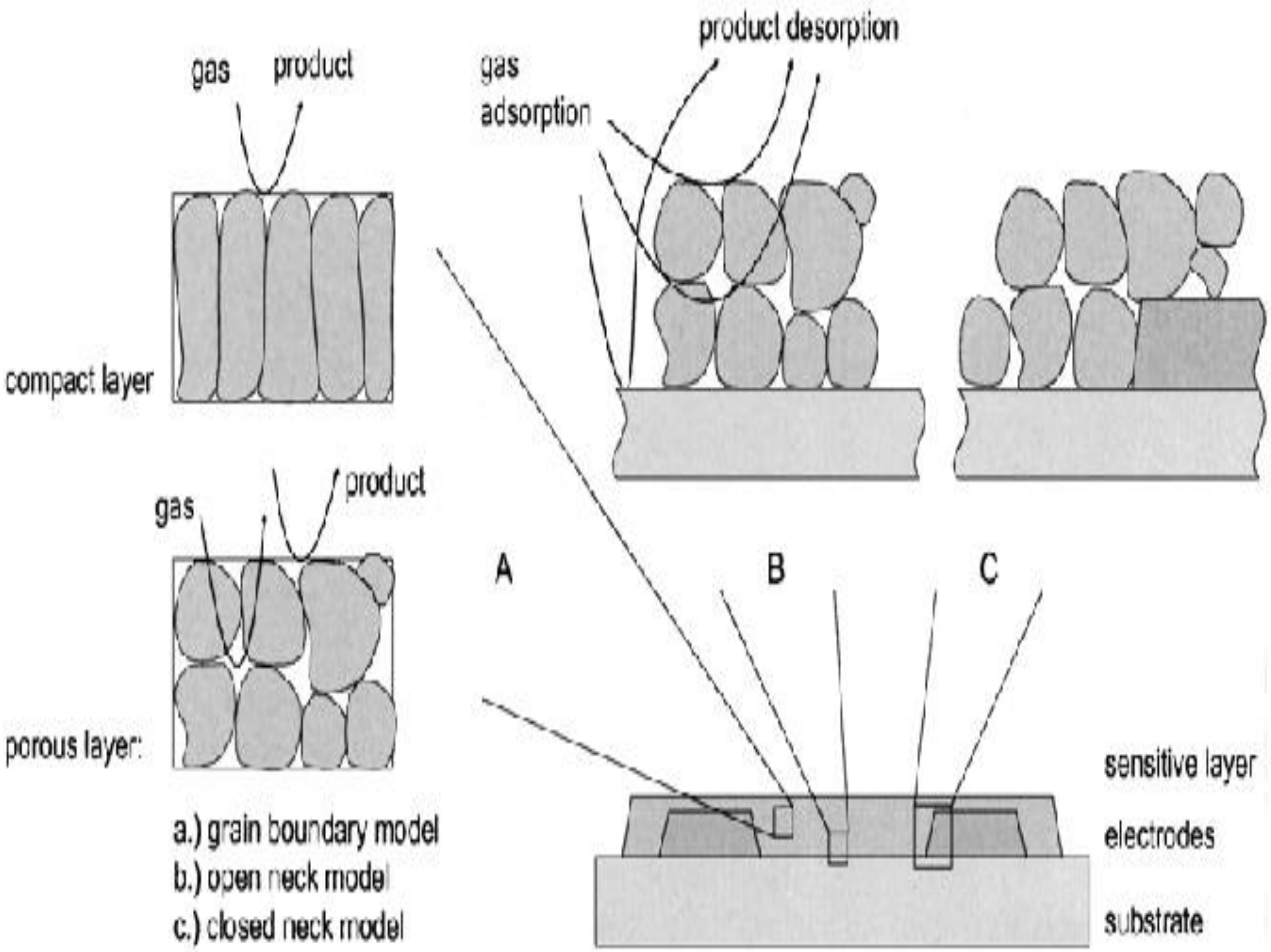
Studies on n- and p-type oxide semiconductor gas sensors
(internet search of Web of Knowledge)

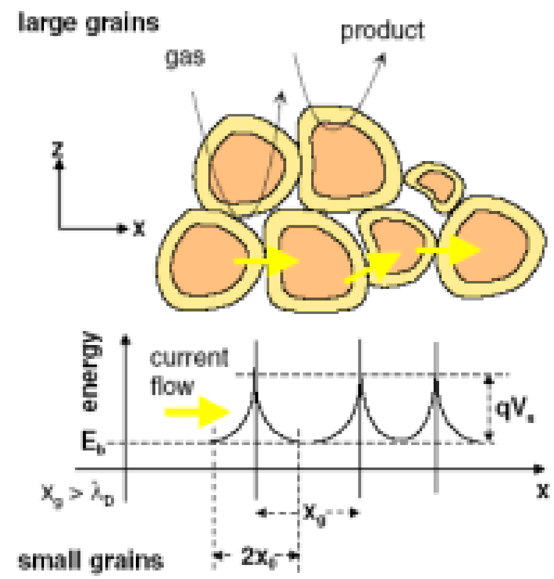


Sensors and Actuators B 192 (2014) 607–627

Metal Oxide Conductometric (resistive) gas sensors

Schematic layout of a typical resistive gas sensor





Conduction models of MOX

*Nicolae Barsan & Udo Weimar, J of Electroceramics, V7, p 143-167, 2001

cost
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Why Ozone Sensor???

- Ozone O_3 is an **powerful oxidazing gas**
- O_3 is widely used for **purification, deodorizing in pharmaceutical, food, chemical industries etc**
- The exposure to O_3 becomes **hazardous to human health** and can cause serious health problems (e.g. headache, burning eyes, lung damage etc)
- The European Guidelines (2002/3/EG) recommend avoiding exposure to ozone levels above 120 ppb.
- Exposure of 0.1 – 1 ppm causes headaches, burning eyes etc (an individual remaining in a 0.1 ppm O_3 environment for two hours will sustain a loss of 20% in breathing capacity, and after remaining in 1 ppm O_3 for 6h)
- O_3 is also produced in the office environment by photocopies and laser printers

Ozone is an important gas

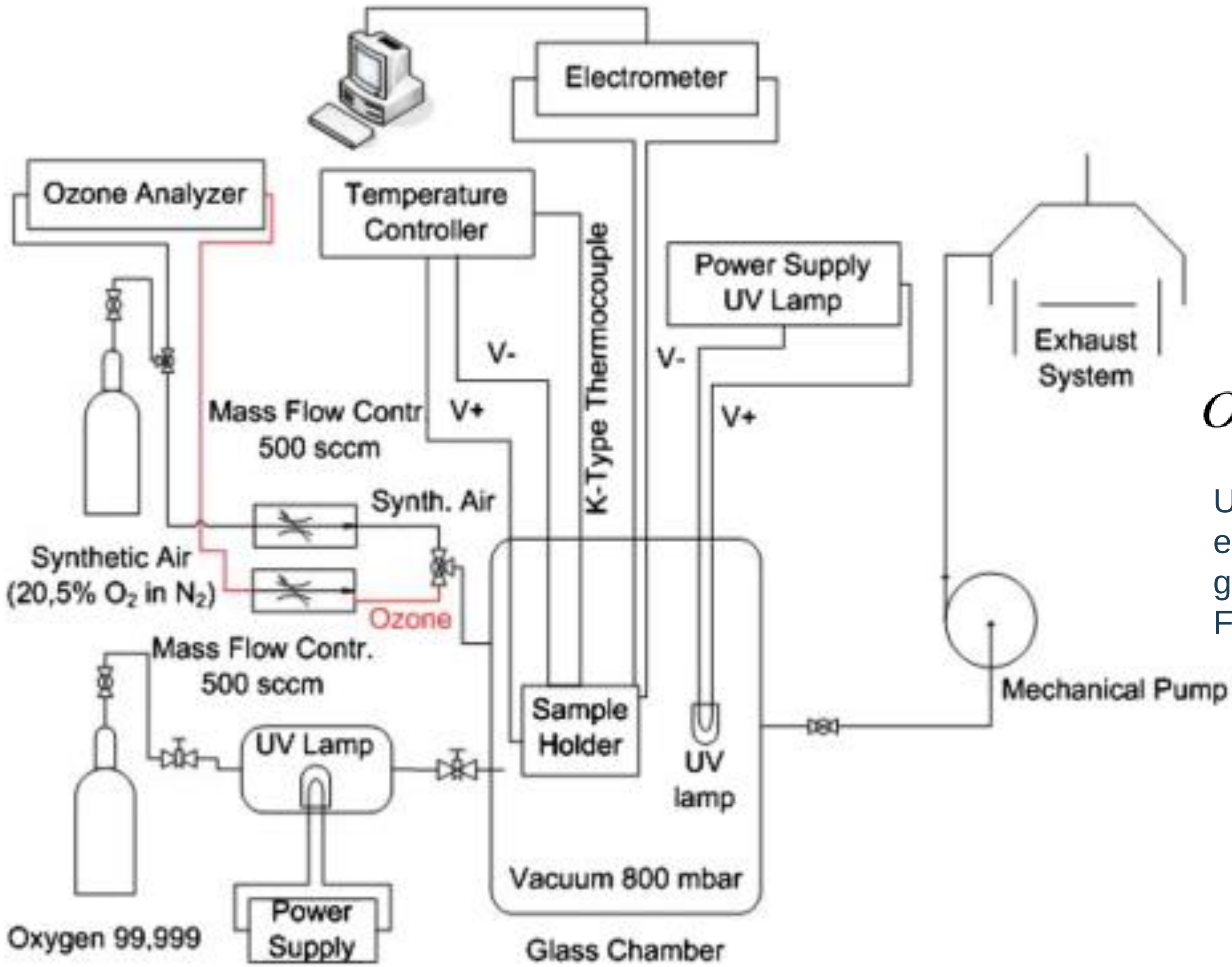
for monitoring and control from ppb to ppm levels

Research activities on Gas Sensors

- **Gas Sensing** elements based on non-Stoichiometric metal oxides (In, Zn)
- **Growth** of Metal Oxide films using; Sputtering, aqua chemical growth, Spray (pulsed –aerosol) Pyrolysis, PLD techniques and solution based techniques (such as printing)
- **Full characterization** of film properties (Structural, Optical, Electrical)
- **Ultra low** detection limits at room temperature (RT) for O3 (< 6 ppb)
- **Ageing effect** and **Durability testing (**Very high sensing response after 7 years)

Conductivity based system

for photoreduction and oxidation processes



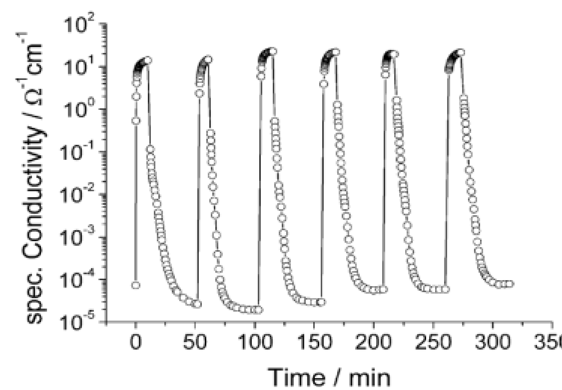
Conductometric Response

Photoreduction and oxidation mechanism: Formation and Annihilation of Vo

$$O_0 \leftrightarrow V_0^{\cdot\cdot}\mu + 2e' + 1/2O_2(g)$$

UV Irradiation with E > bonding In-O energy O atoms transform from bound to gaseous state

Formation of doubly charged O vacancies



Gas Sensing Elements

based on In and Zn

Vacuum 86 (2012) 495–506

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Ultra-low gas sensing utilizing metal oxide thin films

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Keywords:
Metal oxide
Gas sensor
Thin films
Sputtering
Aerosol spray pyrolysis
Conductivity
Surface acoustic waves
Ultra low ozone sensing

A B S T R A C T

The structure, functionality and sensing response of metal oxide films is discussed with emphasis on ZnO and InO_x prepared by Aerosol Spray Pyrolysis in ambient atmosphere and DC Magnetron Sputtering techniques under vacuum. Optical, structural and electrical characterization techniques applied for the in-depth analysis of the film properties are described. Sensing response towards ozone is presented utilizing a conventional conductivity technique as well as surface acoustic wave (SAW) structures and devices. It is shown that sensing responses of extremely low ozone concentrations in the range of a few parts per billion (ppb), at room temperature (RT), may be obtained by appropriate control of the film nanostructure. It is also shown that InO_x employed as sensitive layer on top of surface acoustic wave structures can lead to strong frequency shifts for low concentrations of NO_2, H_2 and O_3 gases.

1. Introduction

Gas sensors have been extensively used to detect and monitor a wide variety of volatile and other radical gases. In particular, gas sensors have a huge variety of applications such as in environmental quality control, public safety, medical applications, automotive applications and for air conditioning systems in aircrafts, spacecrafts, vehicles, and houses [1–6]. According to a recent industrial market report, in the USA the demand for sensors increased with an average annual growth rate 1(AAGR) of 4.6% from a market value of $6.1 billion in 2004 to $7.6 billion in 2009 [7].

Semiconducting metal oxides (MOs) such as SnO_2, TiO_2, InO_x and ZnO are used for gas sensing applications due to the sensitivity of their electrical conductivity to the ambient gas composition, which arises from charge transfer interactions with reactive gases such as O_2, NO_x, CO, hydrocarbons (HC), volatile organic compounds (VOC) and ozone (O_3) [8]. Ozone is a strong multi-purpose oxidizing gas which plays a fundamental role in the formation of photo-chemical smog in urban polluted areas [9]. It may also be met in a wide field of industrial and agriculture applications. Ozone, in concentrations over the 40 ppb threshold, is known to be harmful to the human body according to existing USA Federal Drug Agency and EU standards [10]. Thus a big thrust, for the development of gas sensors, driven by the need to improve the detection of radical gases, including ozone, and trace element detection limits for security and environmental reasons, has emerged. The sensitivity and response time of MO- based ozone sensor films strongly depend on the porosity of the material used. In addition, the grain size of the polycrystalline MO film has also a noticeable effect on its gas sensing properties. However, the gas sensing mechanism of polycrystalline MOs films is only partially understood and the effect of grain size on the gas sensitivity requires further clarification [11].

In the present work the emphasis is on the recent trends to develop ozone sensors fabricated mainly by InOx and ZnO polycrystalline films utilizing two of the most intensively studied techniques, i.e. Aerosol Spray Pyrolysis (ASP) [12,13] and DC magnetron sputtering [14–17]. The influence of the grain size and the surface morphology from films obtained by the above different deposition techniques, achieving sensing responses of the order of a few parts per billion for ozone at room temperature, are reported. A study of the sensitivity of MO films to other harmful gases (NO_2, H_2 and volatile organic vapours [18]) will also be reported.

Structural and ozone-sensing analyses carried out, particularly on InO_x thin films (with a thickness of the order of 100 nm) grown by dc magnetron sputtering onto glass, Si and flexible (PET) substrates, are of interest [19] The reason for involving flexible substrates is that their successful application may lead to simpler,

* Corresponding author. Transparent Conductive Materials Lab, Institute of Electronic Structure and Laser, Foundation for Research and Technology Hellas, 100 N. Plastira str., Vassilika Vouton, 70013 Heraklion, Crete, Greece. Tel.: +30 81 391 271/2; fax: +30 81 391295.
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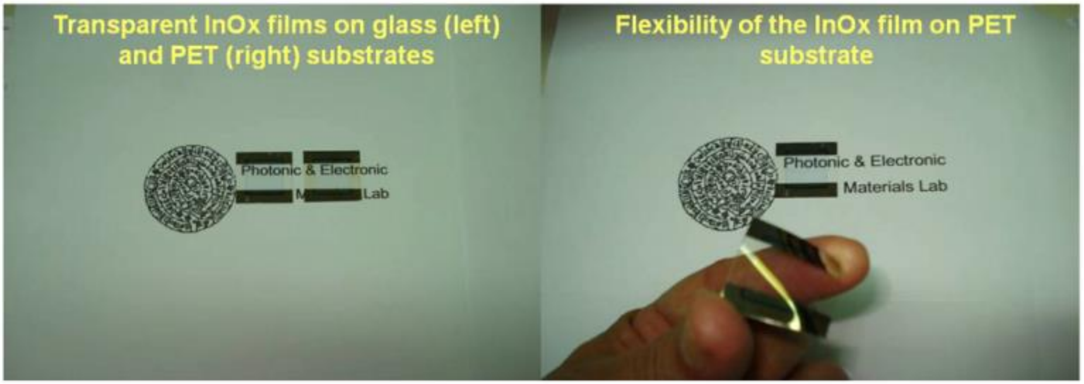
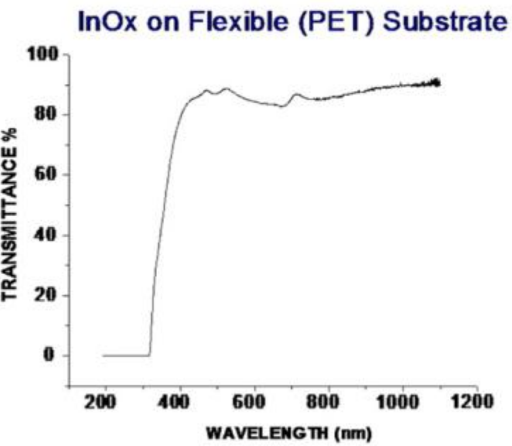
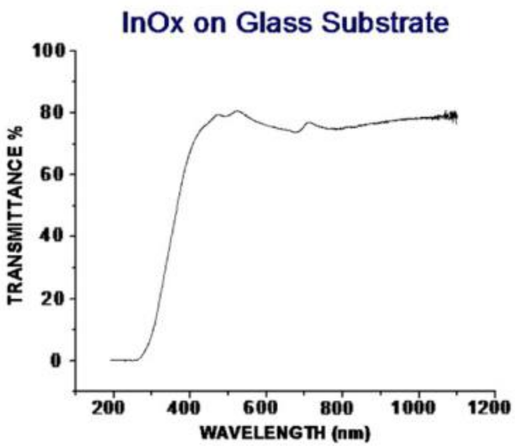
doi:10.1016/j.vacuum.2011.10.013

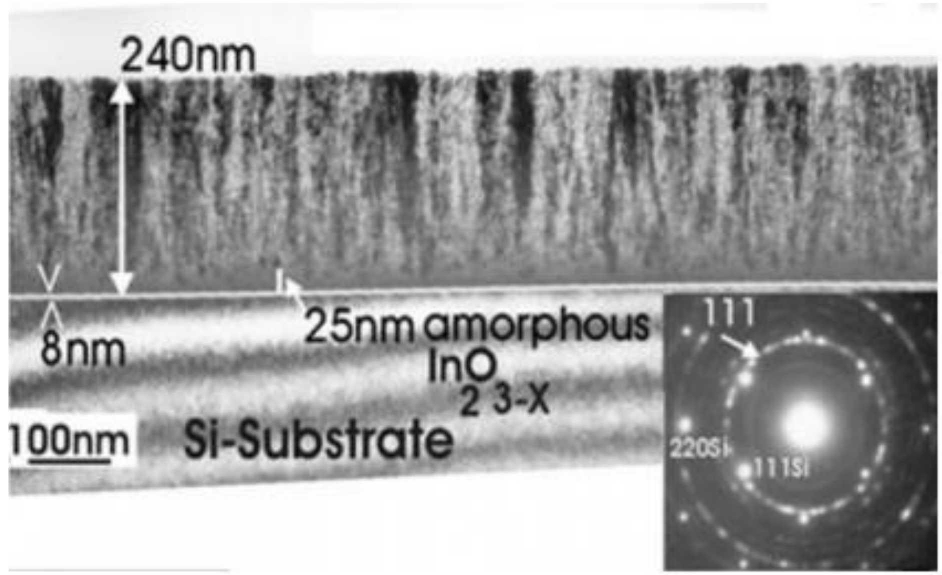
Gas Sensing Elements

In2O3-x on glass and flexible substrate





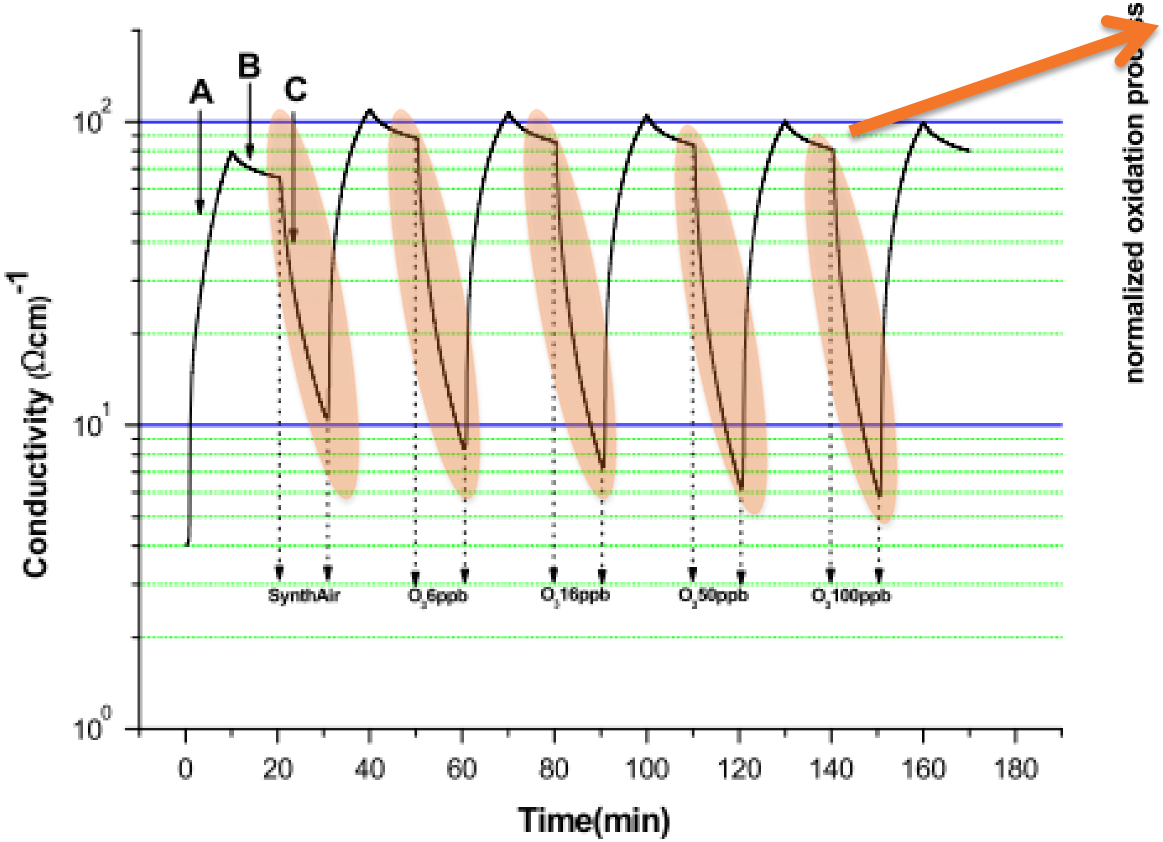


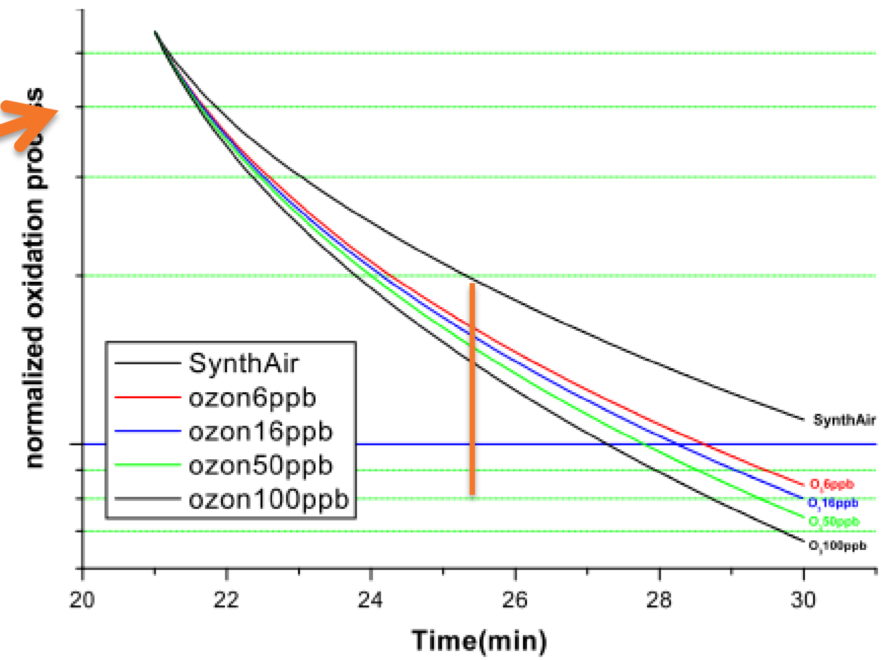


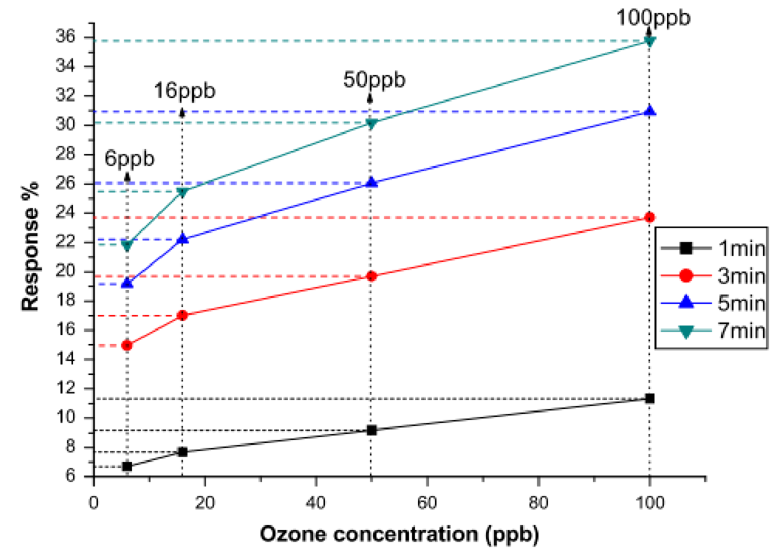
Gas Sensing Elements

In2O3-x on glass and flexible substrate

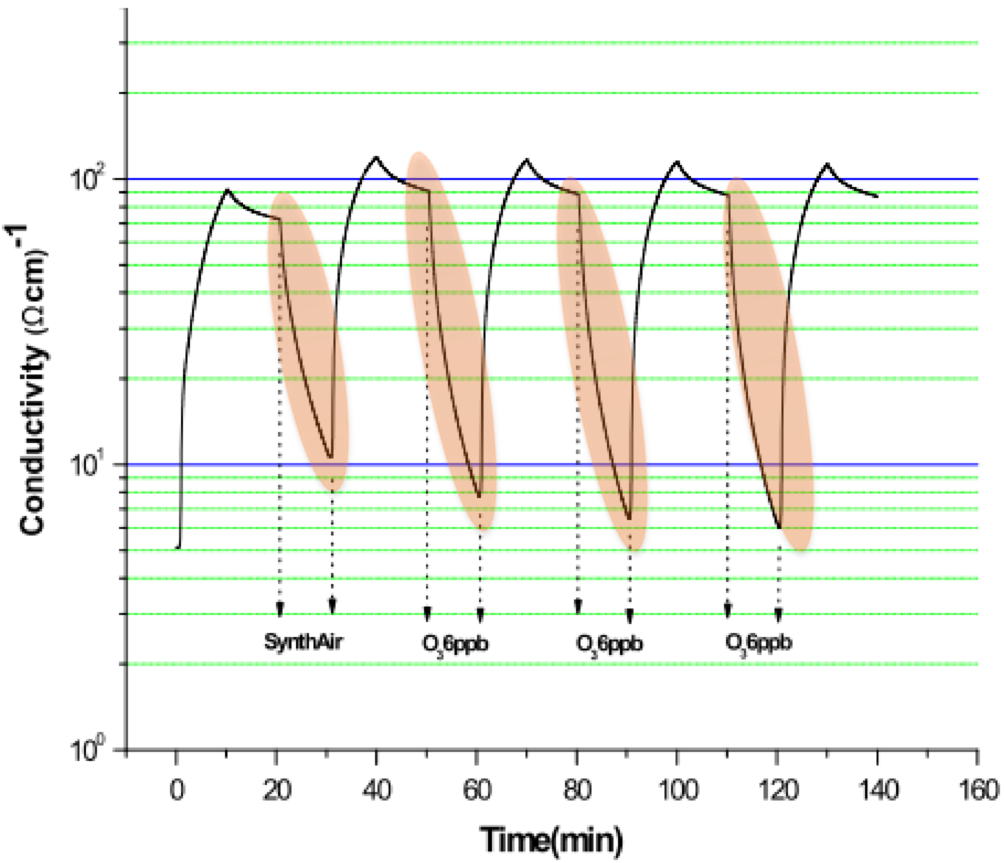
Photoreduction / Oxidation process

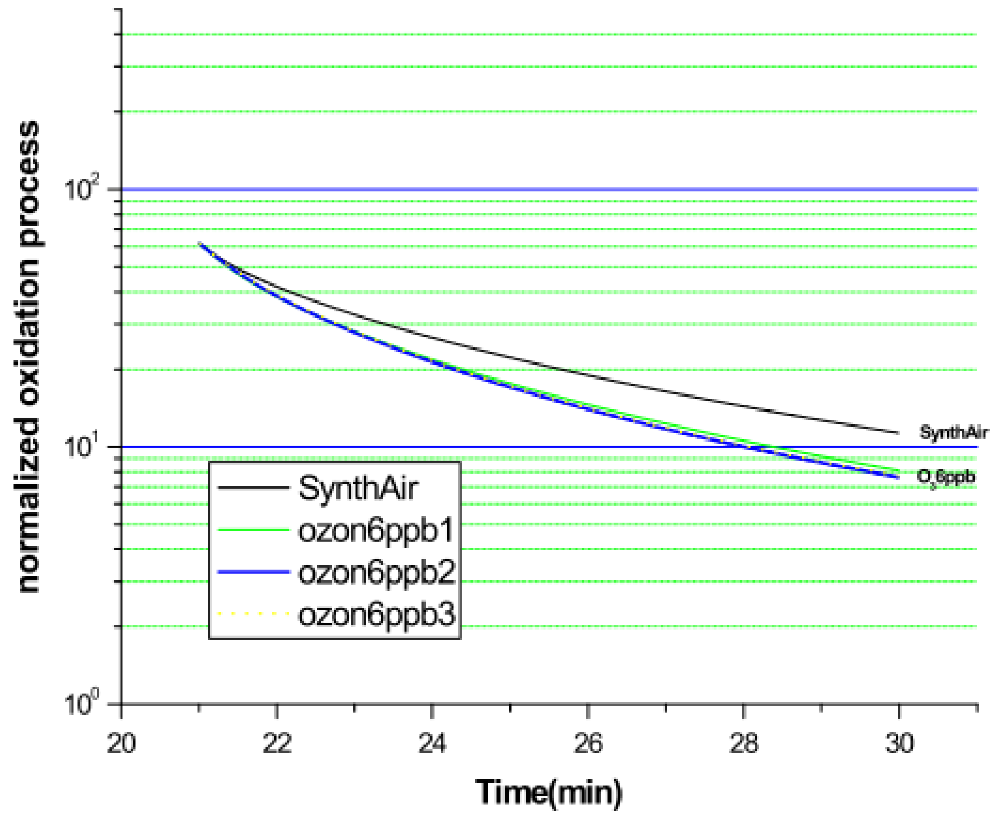






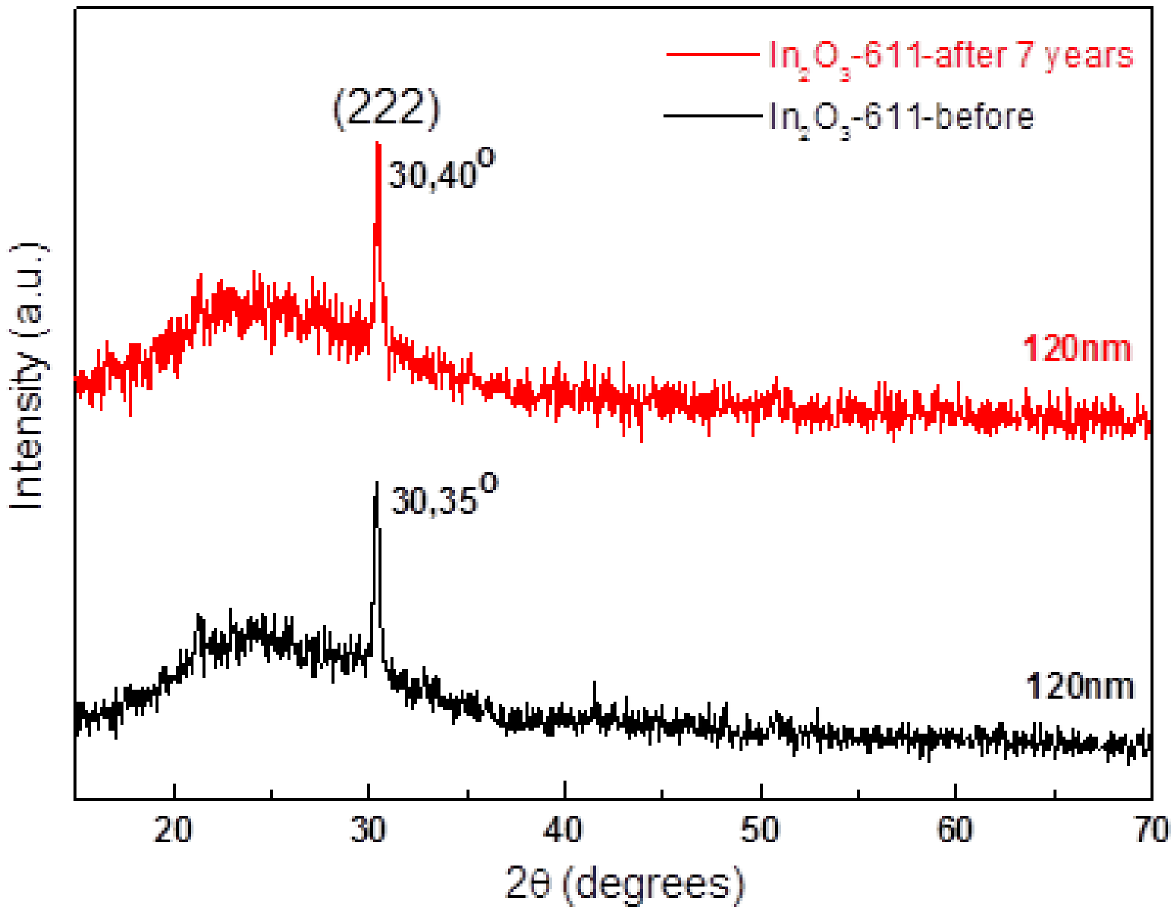
Sensor repeatability towards 6ppb ozone

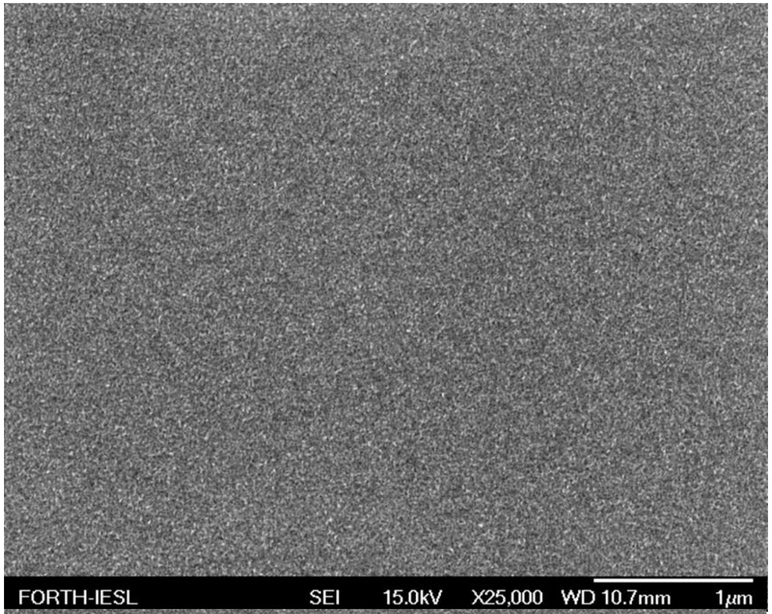




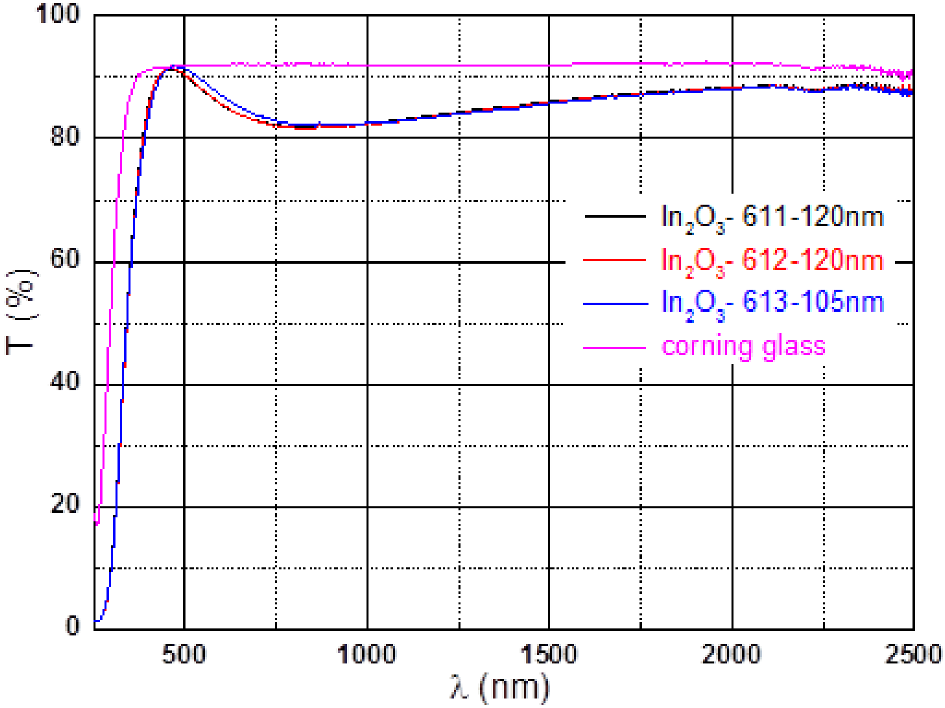
Gas Sensing Elements

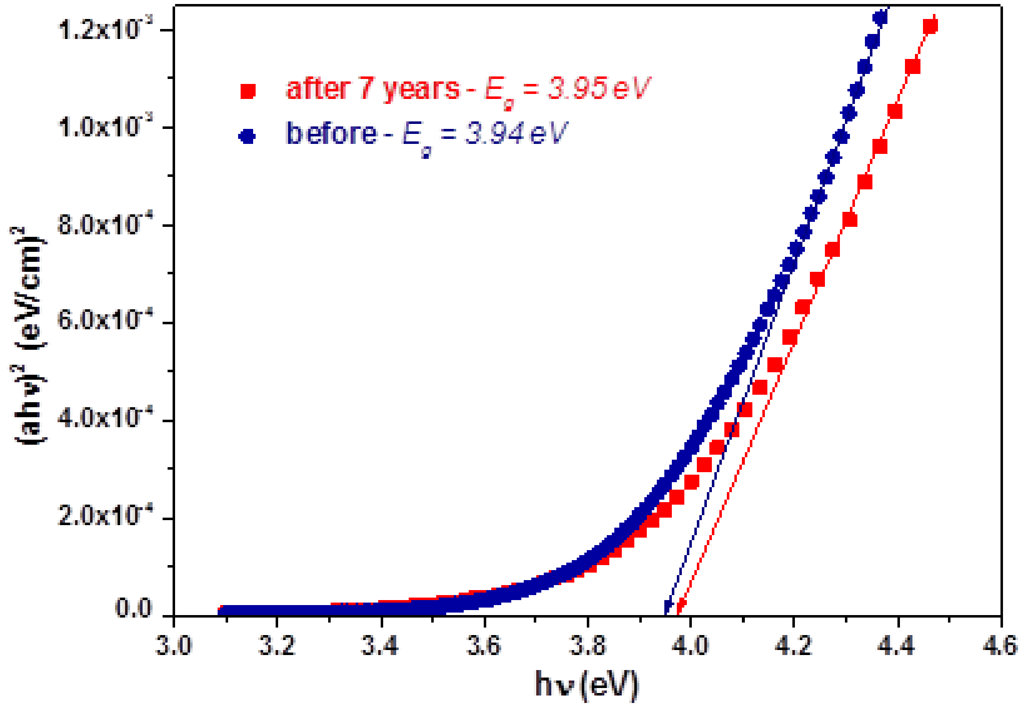
Ageing effect of In2O3-x





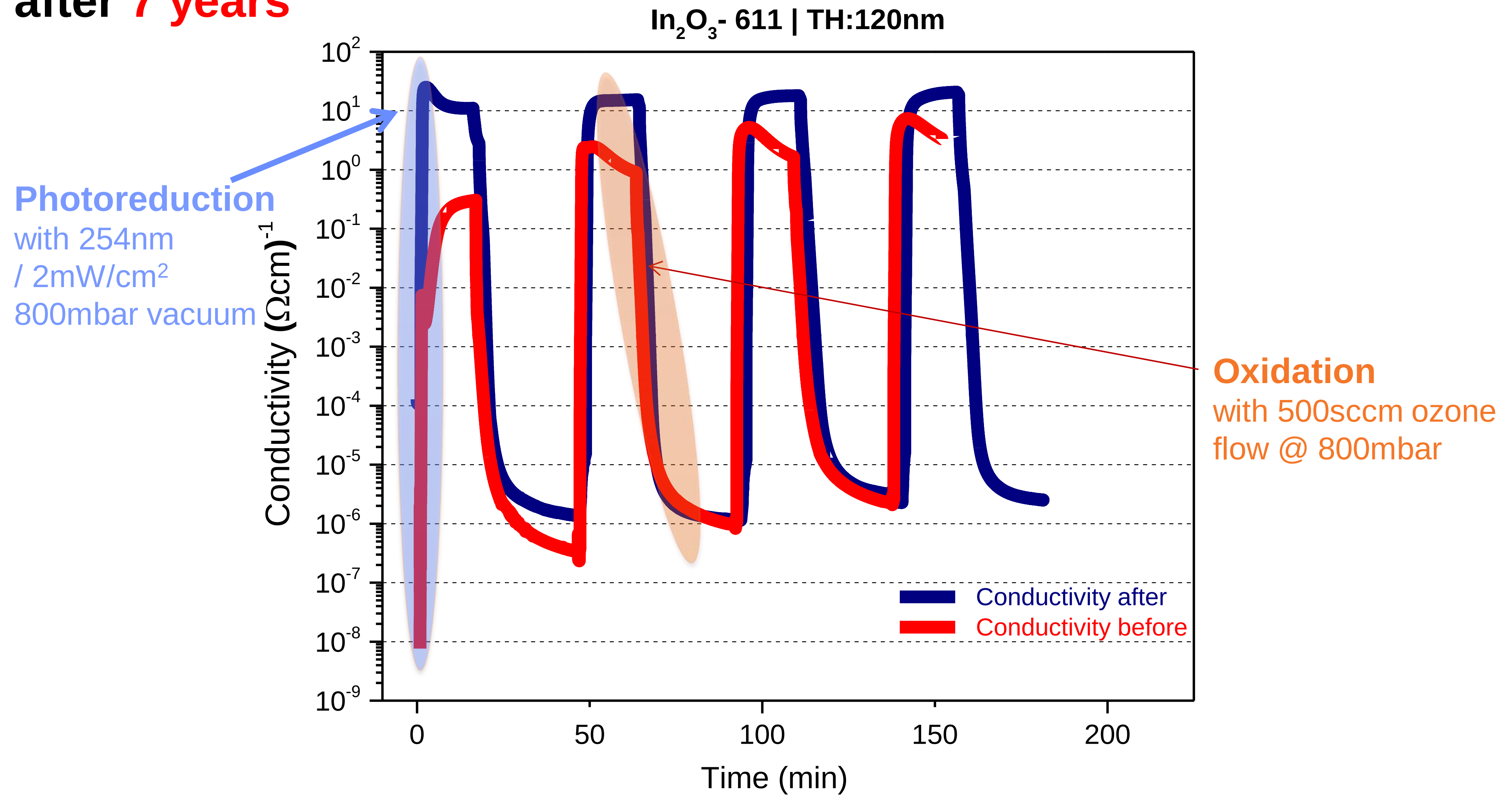
Ageing effect of In2O3-x





Sensing material durability test

after 7 years



Conclusions

- **Gas Sensing** elements based on non-Stoichiometric metal oxides (In, Zn)

- **Ultra low** detection limits at room temperature (RT) for O3 (< 6 ppb)

- **Ageing effect** and **Durability testing (**Very high sensing response after 7 years)

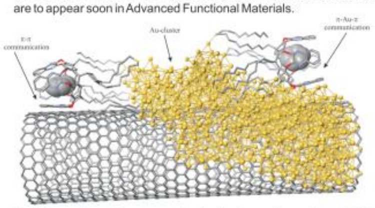
EuNetAir Newsletter COST Action TD1105 Iss. 6/Jun 2015
Iss. 6/ Jun 2015

Focus On

Functional nanomaterial for the molecular recognition of benzene

E. Llobet, MC Member, University Rovira i Virgili, Spain

Exposure to benzene vapors, even at trace levels (e.g. between 10 and 100 parts per billion), may eventually result in serious hemotoxic effects in humans. The group of Prof. Llobet (URV) in collaboration with the Institute of Chemical Research of Catalonia has developed a functional nanomaterial for the molecular recognition of benzene in the ambient. It consists of cavitands anchored to gold nanoparticles that decorate the outer wall of multiwalled carbon nanotubes. The cavitand is a quinoxaline bridged resorcin arene, which is a container-shaped molecule with a cavity that has a shape and size suitable for hosting a benzene molecule. When a guest molecule from the surrounding chemical environment (e.g. benzene) bounds with the cavitand, the electrical resistivity of the carbon nanotube to which the cavitand is attached changes. By using mats of such nanomaterial deposited onto interdigited electrodes, resistive sensors with unprecedented high sensitivity to benzene have been developed (the limit of detection in the part per trillion level). Sensors are fully reversible at room temperature and show promise for being integrated in hand-held portable analysers, wearable detectors for potential application in environmental monitoring. A patent has been filed and these results are to appear soon in Advanced Functional Materials.



The figure shows the communication between the cavitand (with a benzene molecule host) and the Au-decorated carbon nanotube.

Real scale application of novel photocatalyst in tunnel and monitoring the air with sensor control systems

V. Binas, G. Kiriakidis, MC Member, FORTH, Greece

TCM Group at FORTH currently produces in a semi industrial scale a novel photocatalyst to improve air quality. The amount produced for the specific application in a road tunnel in Crete, Greece, was 80 kg of the final product. It has been shown that the material retained the same structural characteristics and photocatalytic activity as in the lab. The full amount of material synthesized was used for the production of 1000 lt (1 t) of TCM "PhotoCat Tunnel" paint, which consequently was applied in December 2014 in a first real scale application of photocatalytic material in Crete to coat the interior surface of a road tunnel (just outside Stalida in Crete) in the framework of a European project (INTERREG) utilized by the Region of Crete. The total surface area that the TCM "PhotoCat tunnel" was applied on was 4000 m2 as shown in the figure. Gas sensor systems have been installed inside the tunnel to monitor the air quality in the tunnel for one year.

Modelling the response of acoustic piezo-electric resonators in biosensor applications

M.Voinova, Chalmers University of Technology, Sweden

Acoustic piezoelectric resonators are widely used as precise analytical chemistry tools for the real-time monitoring of a negligibly small amount of surface-attached mass of biological components, in particular, in environmental biosensor measurements. The surface acoustic wave (SAW)-based sensors and the quartz crystal microbalance (QCM) compared in our work belong to the leading group due to their considerable advantages. These piezoelectric resonators are considered now as high-resolution analytical tools allowing researchers to discriminate between components due to the selective polymer coating on the resonator surface. The gravimetrical measurements performed with the SAW-based or QCM sensors provide the experimental data with high precision for the detection of surface mass for the thin adsorbed layer rigidly attached to the oscillator surface. The new challenge is the analysis of soft and biological materials, where the viscous losses of energy can essentially influence measured characteristics. Modelling is the important part of the analysis allowing researchers to quantify the results of the experiments. The present work provides a general theory of SH-SAW devices probing soft and biological materials. The results are compared with QCM-D operated in liquid media

(M. Voinova, Modelling of the response of acoustic piezoelectric resonators in biosensor applications – Part 1: The general theoretical analysis, J. Sens. Sens. Syst. 4 (2015) 137-142)

GY

EuNetAir Newsletter COST Action TD1105 Iss. 3/Dec. 2013
Iss. 3/Dec 2013

Science & Tech Talk: STSM reports

n- and p- type sensing metal oxides

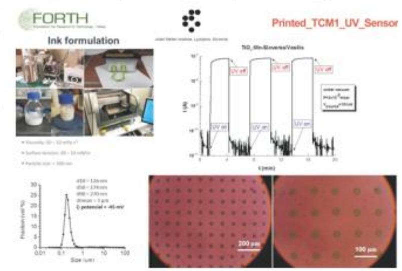
V. Binas

I am a post doc researcher at the Institute of Electronic Structure and Laser in Greece. A short term scientific mission in the framework of the COST Action TD1105 EuNetAir allowed me to visit the Electronic Ceramics Department at Jozef Stefan Institute on September with special focus on ink development of functional metal oxides for advanced gas sensors.

It was an excellent opportunity for me to deepen my knowledge and share experiences about characterization of materials and printable equipment which is essential for the further development of my research activities. This is a first visit in the Jozef Stefan Institute in Slovenia, and based on this, we have started to collaborate in this field. During my short term mission, I learned a lot about ink development (characterization of particle dispersions, formulation, and inkjet printing) and formulation of particle size dispersions for inkjet printing.

All I learned is very important to expand my research activities in new deposition and characterization techniques for n- and p- type metal oxide nanoparticles in different solutions and application of inkjet printing, in the next generation of gas sensor materials. When returning to Crete, I brought not only several printed surfaces on different substrates and know-how with me, but also a bunch of new ideas and many contacts that will be valuable for future cooperation.

Overall, the STSM was very successful. I am deeply grateful to COST Action TD1105 for making this fruitful STSM possible. I would also like to thank my hosts Prof. Barbara Malič, Danjela Kuščer, Oleksandr Noshchenko at JSI and my collaborator at FORTH, Prof. G. Kiriakidis. Snap-shots of my visit and results are presented hereby:



Evaluation of adour impact, caused by industrial sources, through an integrated approach

M. Brattoli

I am a researcher of the Chemistry Department of Bari University (Italy) and my research activity is focused on odor emissions and on all the aspects linked to olfactory pollution: monitoring and control, methodologies and technological solutions, impact evaluation and regulation. The opportunity to apply a STSM in the laboratory of Prof. Anne-Claude Romain at Liegi University and to visit Odometric s.a., the spin-off of the research group, was a great experience for my job training. In fact, during the STSM period, I deepened and learned about some aspects relating to my topic and I was involved in many activities regarding the research aspects and the direct applications of them on the territory. In particular, I focused my attention on electronic noses, developed by Prof. Romain's research group, and I had the opportunity to visit different installations there and to evaluate the scientific results obtained by their devices. Moreover, I was involved in the field inspection method for the evaluation of odor impact through sensorial detection and in olfactometric measurements, performed by an olfactometer that works with a different method related to that I use. Finally, the exchange of knowledge and experiences revealed several aspects for planning concrete collaborations between the two research groups, based on common projects.

Cambridge Air Pollution Sensor Network

M. Müller

I spent three weeks at the Department of Chemistry of the University of Cambridge, UK, in September 2013 (group of Prof. Rod Jones). This lab is strongly engaged in the development and operation of wireless sensor networks for atmospheric pollution monitoring.

First, the STSM provided me with additional insights into state-of-the-art sensor networks including aspects of technology and operation. Second, I initiated the work on a land-use regression (LUR) model utilizing CO data of a temporary sensor network in Cambridge. This network was in operation for two months in 2010. The modelling is still in progress. However, encouraging preliminary results have been achieved. An in-depth analysis of the obtained results is required in order to further improve the applied statistical modelling techniques and the incorporated explanatory variables.

The visit in Cambridge was of great value for me. I especially appreciated the numerous discussions with the colleagues of the host institution and their support. The collaboration with the Cambridge group in the field of LUR modelling will continue.

Acknowledgments

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

Prof. G. Kiriakidis

Dr. E. Aperathitis

K. Moschovis, PhD

M. Gagaoudakis, PhD

TCM Group members

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