

Project III.1A MECHANICAL AND CHEMICAL SENSORS

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Objectives:

- Development of micromachining processes for the realization of novel chemical and mechanical sensors.
- Development of low power silicon sensors based on new materials and new processes.
- Design, fabrication and testing of microsystems using silicon sensors.
- Realization of sensors for specific industrial applications with emphasis on medical, food and automotive fields.

Funding:

- Micro2DNA (IST-FP6-STREP) Contract No 027333, 1/2/2006-31/5/2009
- GSRT-PENED 03ED630, 11/2005-6/2009
- Lab-on-chip, Corralia, National Funds and European Regional Development Funds, NSRF 2007–2013, 1/11/2009-31/10/2012

MAIN RESULTS IN 2009 :

In 2009, our main activities were focused on the following tasks:

- A. Low power Metal-Oxide (MOX) Chemical Sensors
- B. Polymer based chemical sensor arrays
- C. Capacitive Type Sensors

A. Low power Metal-Oxide (MOX) Chemical Sensors*

R. Triantafyllopoulou and C. Tsamis

Solid state chemical sensors are one of the most common devices employed for the detection of hazardous gases, like NH_3 , CO and NO. Their principle of operation is based on the changes of the conductivity of a sensitive material, which is deposited between two electrodes, due to the adsorption of reducing or oxidizing agents onto its surface.

During this year, we continued and completed our research activities on gas sensors for food safety and quality applications as well as for environmental monitoring. The sensors are based on suspended Porous Silicon micro-hotplates. Porous Silicon provides improved thermal isolation, thus reducing heat dissipation to the substrate. For further reduction of power consumption, various methodologies have been developed, such as alternative measuring techniques to constant temperature operation, such as pulsed-temperature mode.

The sensitive material was developed with two alternative technologies: (a) sputtering and (b) microdropping. In the first case thin films were prepared by reactive r.f. magnetron sputtering using a 99.9% pure SnO_2 target. In the second case sensitive materials are prepared by a sol-gel solution with metal additives, in order to enhance its sensitivity, and then deposit the additive-modified nanostructured metal oxides on micro-hotplates, by microdropping (Fig.1a). In this way, the use of Porous Silicon micro-hotplates allows for the fabrication of sensor arrays (Fig. 1b) that incorporate varying sensitive materials, while at the same time they exhibit a significant reduction of the power consumption.

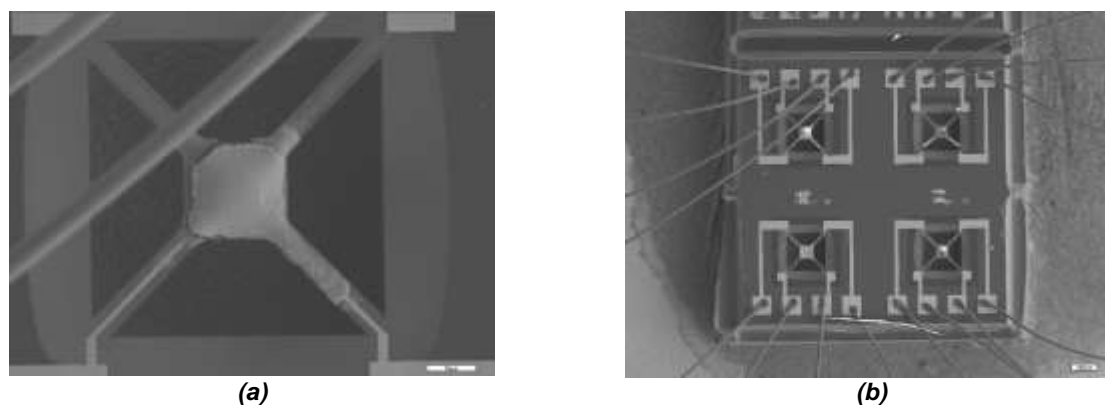


Fig. 1. SEM image (a) of the $\text{SnO}_2\text{:Pd}$ deposited on a micro-hotplate using micro-drop technique and (b) of a sensor array with micro-dropped nanostructured sensitive materials $\text{SnO}_2\text{:Pd}$ and $\text{WO}_3\text{:Cr}$, mounted on a package.

Sensors were characterized in various ambient (CO , NO , NH_3) using two alternative methodologies: (a) isothermal mode operation and (b) pulsed mode operation, for gas concentrations ranging from 10 to 500 ppm. Typical response of sputtered SnO_2 gas sensors towards CO is shown in fig. 2a, for isothermal mode. Operation in pulsed temperature mode, results in higher sensor sensitivity and enhanced selectivity, with reduced power consumption. In this case, the sensitivity and selectivity of the sensors was estimated as a function of the total shape of the pulse cycle, the duration of the pulses and the temperatures of the “hot” and the “cold” part of the measuring cycle. In Fig. 2b the response of micro-dropped $\text{SnO}_2\text{:Pd}$ gas sensor is shown for two different cycles. Improved results are obtained compared to isothermal mode, the enhancement being larger as the low temperature of the pulsed temperature cycle reduces.

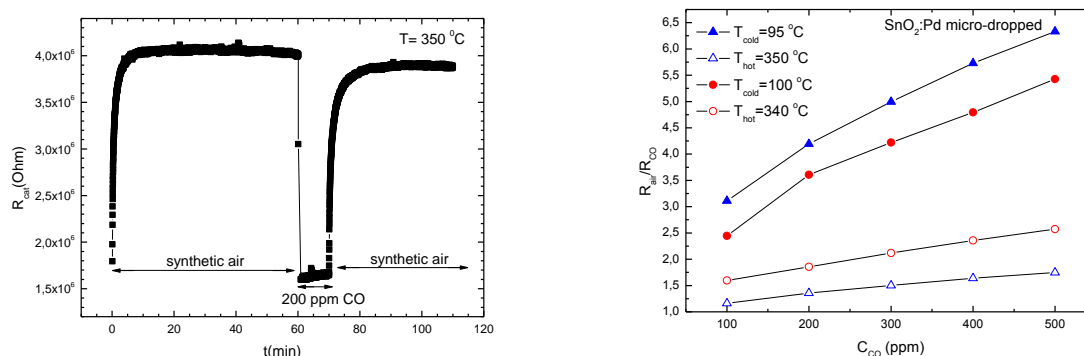


Fig. 2: (a) Typical response of gas sensors with sputtered SnO_2 towards detection of 200 ppm CO . (b) Low power operation and CO detection enhancement for micro-dropped $\text{SnO}_2\text{:Pd}$ gas sensors working at various pulsed mode cycles.

B. Polymer based chemical sensor arrays

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Must fermentation is a complex enzymatic process where, apart from the conversion of sugars to ethanol and CO_2 , a variety of organic compounds are produced in orders of magnitude lower concentrations. Control of the fermentation process is critical for the organoleptic quality of the final product. The complex characteristic aroma profile of a wine or a fermenting must, produced by a variety of alcohols, esters, organic acids etc, can be identified with instrumental chemical analysis after proper extraction techniques, which are time consuming and require expensive laboratory equipment.

Our research work deals with the challenging task to monitor the must fermentation progress, and detect possible deviations from optimum fermentation with a gas sensor array, without the use of pre-concentrator steps. To achieve this goal interdigitated capacitors (IDCs) fabricated with $2.0\mu\text{m}$ conventional microelectronic technology and coated with polymeric film were employed. IDC sensor is a mature technology capitalizes on the advances of microelectronics / microsystems processes

offering high yield and low cost systems. For the particular study arrays of 8 IDEs were fabricated and coated with hydrophilic and hydrophobic polymers through a well formatted around the capacitor. The fermentation process of a particular grape must was duplicated under laboratory conditions and monitored in terms of standard chemical analysis and the response of the gas sensor array to the headspace of must samples, on a daily basis. Finally, the sensor array signals were subjected to PCA analysis. The obtained results indicate that the PCA analysis is capable of discriminating the must from the wine. It is also shown that this discrimination is the same for the two fermentations due to same initial chemical composition of both musts at and of the wines produced at the end of the process. Furthermore there is a clear difference from the response of the standard ethanol solutions.

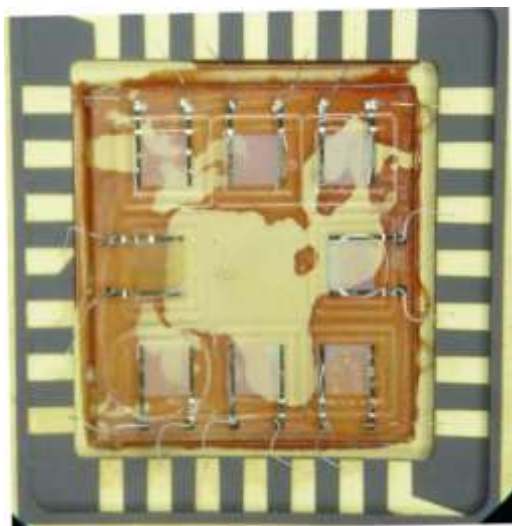


Fig. 3 Optical micrograph of the 8-IDE sensor array coated with different polymers and packaged in a conventional DIL package. Thick (~50 μ m thickness) epoxy well (EPR resist) around every IDC allows reproducible and well defined casting of the sensing polymer layer.

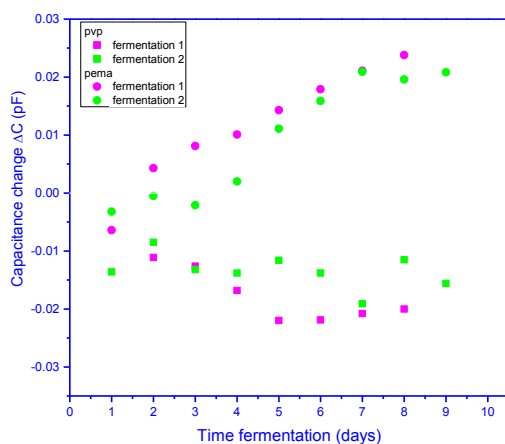


Fig. 4 Responses of selected IDEs coated with PVP and PEMA polymer films. In general in hydrophobic polymers, the responses to the musts increase with increasing ethanol content. Difference between standard EtOH solutions and musts of the same ethanol concentration are assigned to the presence of other volatile compounds in the must

C. Capacitive Type Sensors

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Capacitive DNA Sensors Arrays

A capacitive type chemical/biological sensor array organized in a 16 x 16 sensor matrix has been developed. Each sensor in the array consists of a single crystal silicon membrane which is able to sense surface stress changes which could be exerted by either a chemically sensitive layer or the interaction between immobilized biological species with other target biological species. The array has been tested in the detection of b-thalassemia CD19 oligonucleotides. With these tests it was proven that it is possible to detect the hybridization reaction of the CD19N oligonucleotide by converting the surface stress changes of the ultrathin silicon membrane into a change of the capacitance of the sensor. To verify this, an additional device was fabricated which has exactly the same structure as the capacitive DNA sensor with two modifications: i) no cavity was etched underneath the upper electrode

of the capacitor (this is the ultrathin silicon membrane in the sensor device) and ii) the upper electrode is fabricated out of aluminium material for simplicity. Thus the upper electrode would only check charge changes on its surface and not mechanical changes as it is not allowed to deflect. The experiments have shown that the change in capacitance during hybridization is one order of magnitude lower for the Al-electrode capacitors compared to the capacitive DNA sensors thus proving the original assumption that the capacitive sensor response is due to surface stress changes during hybridization rather than a charge accumulation/shielding effect.



Fig. 5: In order to perform the oligo experiments tight control over the sample temperature is required. Therefore the hybridization cassette was allowed to settle on a hotplate whose temperature could be regulated to within 0.1°C. Furthermore, in order to minimize bubble formation manual pinch valves were introduced in the fluidic circuit thus increasing the control over the flow of the various fluids. Fluid control was achieved using a peristaltic pump at the exit of the fluidic circuit. Finally a relay matrix undertakes the task of switching each sensor in the array to a capacitance meter.

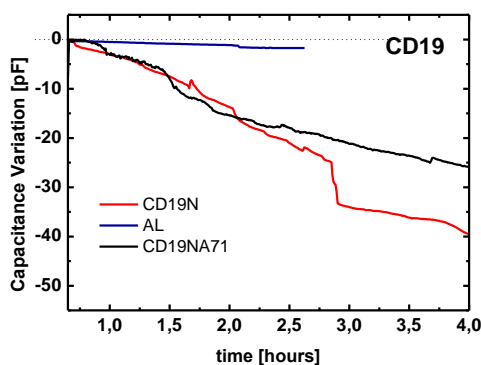


Fig. 6: The average response of the Al capacitors when 36 nM of PCR are under analysis is depicted together with the response of two different capacitive sensor arrays for that same concentration. The change of capacitance for the Al capacitors is negligible when compared with that of the sensors thus excluding that a non mechanical effect is the reason for the DNA sensor response.



Fig. 7. Finished close-up photo of the Al capacitor array device.

PROJECT OUTPUT in 2009

Publications in International Journals

1. "Detection of the Biotin-Streptavidin interaction by exploiting surface stress changes on ultrathin Si membranes", V.Tsouti, C.Boutopoulos, P.Andreakou, M.Ioannou, I.Zergioti, D.Goustouridis, D.Kafetzopoulos, D.Tsoukalas, P.Normand, S.Chatzandroulis, *Microelectron. Eng.*, vol. 86 (4-6), 1495-1498, 2009.
2. "Electrical and optical evaluation of polymer composites for chemical sensing applications", G. Dendrinou, L. Quercia, I. Raptis, K. Manoli, S. Chatzandroulis, D. Goustouridis, K. Beltsios, *Microelectronic Engineering*, vol. 86 (4-6), 1289-1292, 2009.
3. "Novel disposable microfabricated antimony-film electrodes for adsorptive stripping analysis of trace Ni(II)", Ch.Kokkinos, A.Economou, I.Raptis, Th.Speliotis *Electrochem. Comm.* 11 250-257, 2009.
4. "Polymer/BaTiO₃ nanocomposites based chemocapacitive sensors", P.Oikonomou, K.Manoli, D.Goustouridis, I.Raptis, M.Sanopoulou *Microelectron. Eng.* 86 1286-1289 2009.

Publications in International Conference Proceedings

1. "Capacitive sensor arrays with controllable deposition of the sensing polymer area for VOCs applications: Design and measurement considerations", K. Manoli, D. Goustouridis, P. Oikonomou, S. Chatzandroulis, M. Sanopoulou, I. Raptis, *Procedia Chemistry*, vol. 1, issue 1, 176-179, 2009.
2. "Disposable micro-fabricated electrochemical bismuth sensors for the determination of Tl(I) by stripping voltammetry", Ch. Kokkinos, I. Raptis, A. Economou, Th. Speliotis *Procedia Chemistry*, vol. 1, issue 1, 1039-1042, 2009.
3. "Monitoring of must fermentation progress by polymer coated capacitive vapour sensor arrays", P. Oikonomou, K. Manoli, D. Goustouridis, E. Valamontes, I. Raptis, M. Sanopoulou *IEEE Sensors 2009* (Christchurch, New Zealand, 10/2009)

Conference Presentations

1. "Direct laser printing of polymers for gas sensing applications", C. Boutopoulos, C. Pandis, P. Pissis, I. Zergioti, V. Tsouti, S. Chatzandroulis, , COLA 2009 10th International Conference on Laser Ablation, Singapore 22-27 November 2009.
2. "In-situ monitoring of must fermentation by polymer coated interdigitated sensor arrays", P.Oikonomou, K.Manoli, D.Goustouridis, I.Raptis, M.Sanopoulou *Instrumental Methods of Analysis (IMA 2009)* (Athens, Greece, 10/2009)

PhD Theses

1. V. Tsouti, "Fabrication of Si nanocantilevers for efficient chemical detection", conducted at IMEL and NTUA/SEMFE (June 2009)
2. R. Triantafyllopoulou, "Fabrication and characterization of Metal Oxide Chemical Sensors", NTUA/SEMFE (October 2009)

Patents

1. Greek patent bureau (OBI), appl. no. GR20090100300 (2009), "A Capacitive Type Device for Chemical and Biological Sensing And A Method To Fabricate Same", NCSRDI, P.Normand, S.Chatzandroulis, D.Goustouridis, V.Tsouti.