Project III. 2
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:

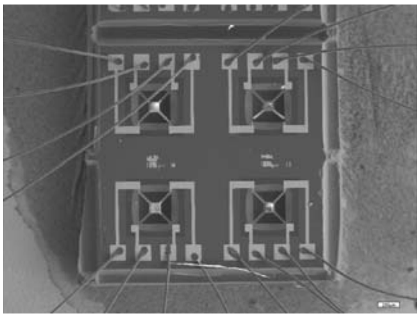
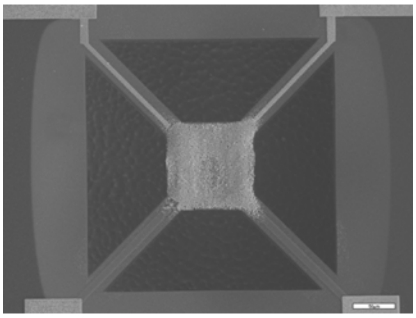
- EU - IST-FP6-STREP-027333 Micro2DNA, "I*ntegrated polymer-based micro fluidic micro system for DNA extraction, amplification, and silicon-based detection*", P. Normand
- EU, IST, IP, GOODFOOD, "*Food Safety and Quality Monitoring with Microsystems*", contract No. 508774, C. Tsamis
- GSRT Greece-Italy bilateral cooperation "*Fabrication and characterization of an array of transparent conductive thin film polymeric composite as multiparametric sensitive layers for a new e-nose*", D. Goustouridis
- GSRT-PENED 03ED630, "*Micromachined chemical sensors for controlling food safety and quality*", C. Tsamis
- GSRT- ENTER 05EP032, "*Development of MOSFET type chemical sensors for wireless sensor networks*", C. Tsamis

RESEARCH RESULTS

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

R. Triantafyllopoulou S. Chatzandroulis, A. Tserepi and C. Tsamis

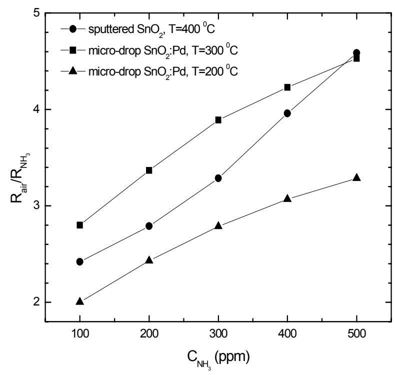
Solid state chemical sensors are one of the most common devices employed for the detection of hazardous gases, like NH_3. Their principle of operation is based on the changes of the conductivity of a sensitive material, which is deposited between two electrodes, due to the adsorption of reducing or oxidizing agents onto its surface. Many techniques have been developed for the deposition of catalytic materials. One of the most widely used techniques is to prepare 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 microdroping (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. Porous Silicon provides improved thermal isolation, thus reducing heat dissipation to the substrate.

(a) ***(b)***

Fig. III.2.1: *SEM image of the micro-drop sensors (a) mounted on a package, after the wire-bonding and (b) the micro-dropped sensitive material SnO_2:Pd*

During this year, we developed gas sensors for food safety and quality applications as well as for environmental monitoring, fabricated by the micro-drop technique. The sensors are based on suspended porous silicon micro-hotplates. Two different nanostructured materials were deposited on top of the micro hotplates using micro-drop technique: a) SnO_2:Pd and b) WO_3:Cr. For the characterization of the SnO_2:Pd and WO_3:Cr micro-drop sensors, measurements in NH_3 ambient took place. The detection of the gas was conducted in isothermal operation mode, which means that the sensors were applied with a constant power. The response of the SnO_2:Pd sensors was measured for high concentrations of NH_3, as it is shown in fig. 2a. Lower concentrations of NH_3 were detected by both SnO_2:Pd and WO_3:Cr sensors, as it is shown in fig. 2b. The gas sensors with micro-dropped sensitive materials and especially SnO_2:Pd exhibit the highest sensitivity towards NH_3, with lower power consumption.



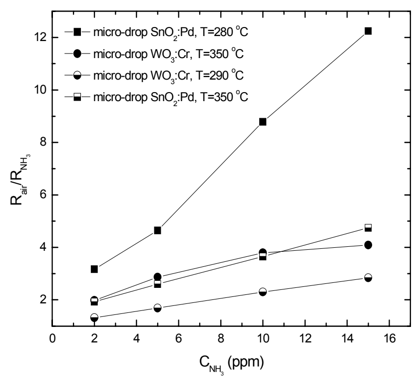


Fig. III.2.2: *(a) Comparison of the sensitivity of gas sensors with undoped sputtered SnO_2 sensitive material and sensors with micro-dropped SnO_2:Pd sensitive material, (b) Sensitivity of gas sensors with SnO_2:Pd and WO_3:Cr micro-dropped sensitive materials, in various temperatures, for low concentrations on NH_3.*

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B. FET-type chemical sensors for wireless applications

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Chemical sensors for wireless applications are of major interest since they turn into reality the possiblity to sense and monitor environmental changes in hard-accessible mediums or even to escort environment-sensitive products (such as food) in order to monitor and build environment-related database. Low-energy consumption (low current operation), room-temperature operation as well as integration in small dimension are some of the most important requirements of such sensors. To this end, we investigate two candidate devices: i) MOS capacitive sensors and ii) FET-type sensors with active catalytic layer. During this year, we focused our efforts on both types of devices.

i) MOS capacitive sensors of Si/SiO_2/Pt and Si/SiO_2/SnO_2/Pt, with thin and thick silicon dioxide layer were fabricated and are about to be tested whether they can effectively sense gas mixtures containing NH_3, H_2, CO, etc. In our preliminary research, it has been found that a correlation between MOS gas sensor and NH_3 is present at room temperature.

ii) Interdigitated bottom-gate FET devices (gasFET) with various channel lengths (from 0.3 μm to 2 μm) were developed (Figure 3). Palladium was used as source and drain electrodes and thin SiO_2 layers as gate insulator. Thin zinc oxide layer was grown with the aid of pulsed laser deposition (PLD) method at room temperature. The above-mentioned fabricated gasFET sensors were tested at CO environment at 200 °C as demonstrated in Figures 4 and 5.

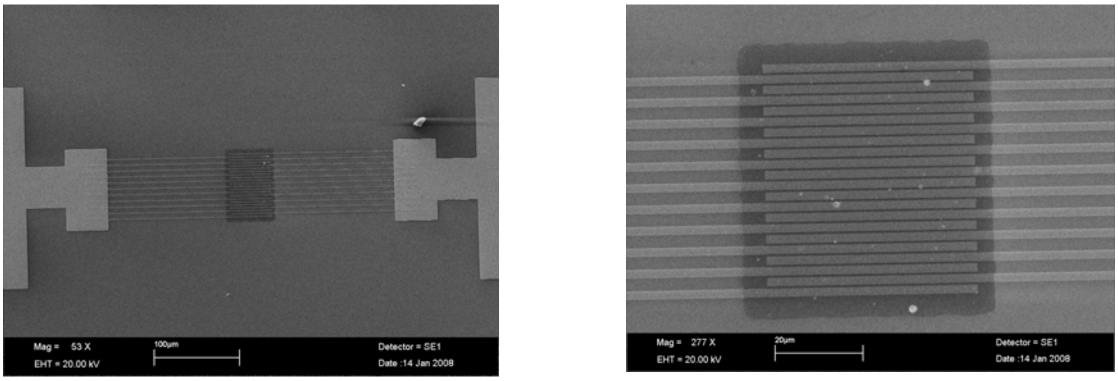

Fig. III.2.3: *SEM images showing the interdigitated source and drain electrodes of the bottom gate FET device.*

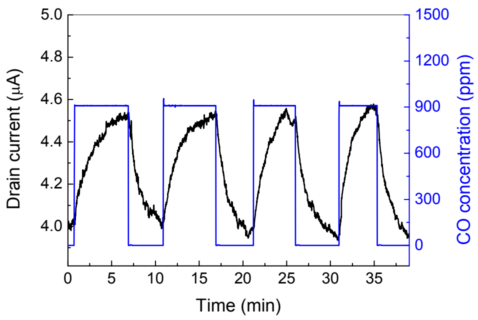

Fig. III.2.4: *Drain current increase at the presence of 900 ppm of CO in dry air at 200 ℃.*

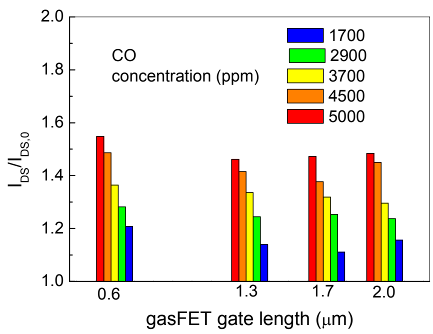

Fig. III.2.5: *Drain current increase depends linearly with CO concentration in dry air, independently of the gate length of the gas FETs. (Measurements at 200 ℃).*

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C. Polymer based chemical sensor arrays

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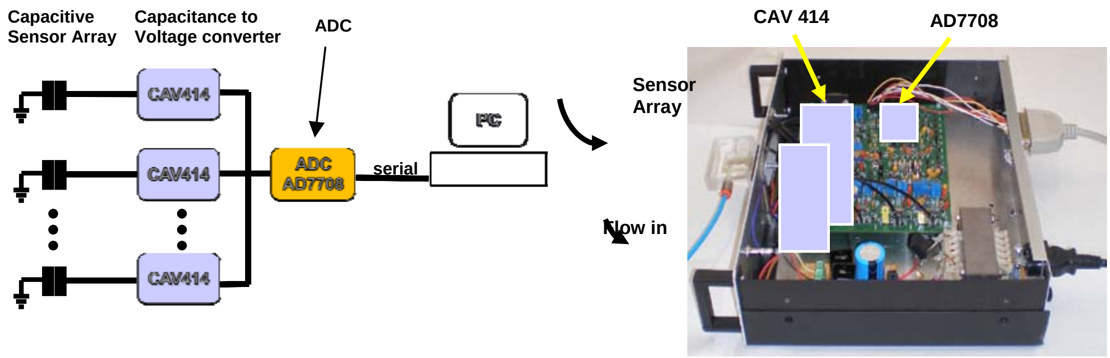
Low power capacitive type chemical sensors using polymer coated InterDigitated Electrodes (IDE) are the focus of this research. An InterDigital Electrode (IDE) chemical sensor may be fabricated by covering the electrodes with a polymer layer. The transduction then relies on the permittivity changes and swelling of the covering polymer, to inflict a change in the capacitance between the two electrodes structure. InterDigital Capacitive (IDC) sensors are perhaps one of the most promising devices in terms of fabrication costs and ease of integration in a standard CMOS process, requiring only minimum post-processing.
In our work a capacitive array of IDC chemical sensors with an electronic interface, which converts capacitance changes into digital signal, has been developed. Photolithographic deposition has been used to apply four different polymer sensing layers (PHEMA, PMMA, EPR, PDMS) onto IDEs fabricated on a glass substrate to minimize parasitic capacitances. The electronic interface is able to handle up to eight capacitive sensors (fig. 6). It is built around a 16 bit analog to digital converter (Analog Devices, AD7708). This chip has 8 input channels, which are driven by 8 corresponding capacitance to voltage converters (CAV414) connected to one of the capacitive chemical sensors in the array.



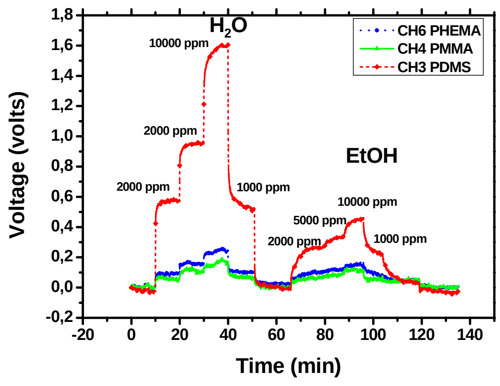


Fig. III.2.6: (*Top Left*) Block diagram of the electronic interface. (*Top right*) Electronic interface and sensor array, homed in a dedicated Plexiglas chamber plugged in position. (*Left*) Response of the system under water and ethanol vapors.

Sensing properties enhancement of polymeric films via irradiation

The use of patternable polymeric films and their subsequent treatment with VUV, DUV irradiation and plasma to engineer individual sensitivities in chemical sensor arrays was proposed and studied. The effect of the treatment on the swelling properties of poly(methyl methacrylate) (PMMA) thin films in certain analytes was studied using White Light Reflectance Spectroscopy. The relative expansion of the PMMA film was clearly found to depend on the irradiation conditions (fig. 7,8) From the treatment methods examined the one with the higher sensing sensitivity amplification (5 times higher in certain cases) was the VUV irradiation. Further studies of the VUV processed areas with AFM, FTIR were carried out in order to reveal the mechanism of this enhanced sensing capability.

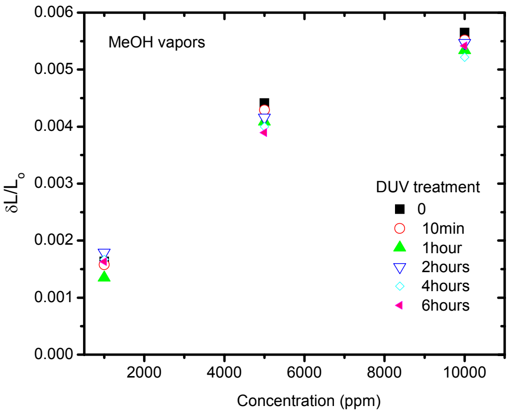


Fig. III.2.7: DUV irradiation effect on the PMMA swelling. Exposures up to 6h did not present any gain in the swelling of the studied vapors

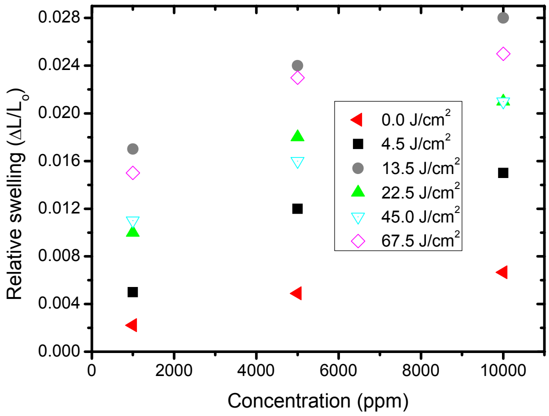


Fig. III.2.8: Relative swelling values of PMMA films for irradiated samples at different VUV exposure doses for methanol vapors.

Conductometric chemical sensors

Conductometric chemical sensors based on polymer composite films, synthesized by adding conductive fillers to the polymer solutions and deposited between two predefined electrodes, are well established. The available methods for deposition of the sensitive composites lack in pattern precision and repeatability. In order to overcome pertinent problems a novel methodology based on conventional patterning methods was developed and applied. The definition of two conductive polymer composites (poly(dimethylsiloxane) /carbon black and epoxy polymer / carbon black areas on the same substrate was demonstrated (fig. 9). The two sensors performance is evaluated and considered as a first step towards the fabrication of a conductometric polymer composite array. Electrical sensitivity is enhanced over dimensional sensitivity, especially for low dimensional-sensitivity cases. In addition it was found that electrical response depends on the exact electrode configuration (fig. 10). Short-circuiting situations can have a substantial effect on the electrical sensitivity of the composites in consideration.

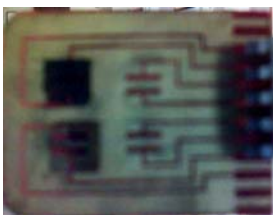


Fig. III.2.9: Photograph of the patterned EPR-CB and PDMS-CB polymer composite sensor pair.

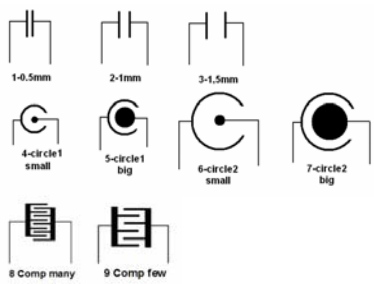


Fig. III.2.10a: Different electrode configurations examined.

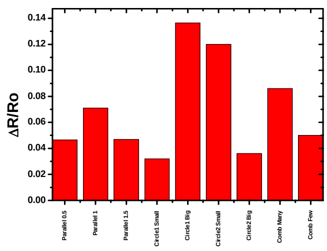


Fig. III.2.10b: Relative resistance change of a PDMS/CB sensor to 5000 ppm of water vapors for the nine different electrodes

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D. Capacitive Type Sensors

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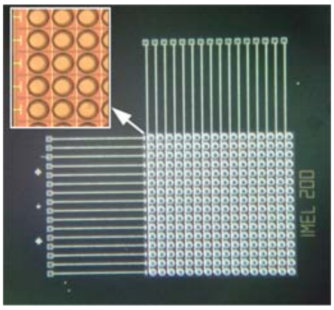
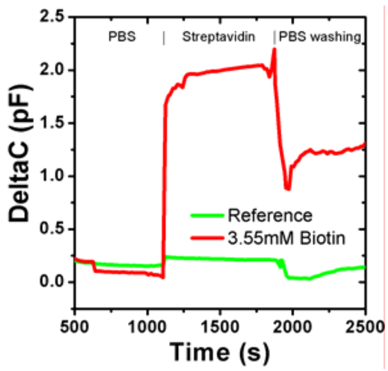
**National Technical University of Athens, **IMBB/FORTH*

Capacitive DNA Sensors Arrays

Unlabeled DNA detection has been the focus of great interest in recent years as it simplifies sample preparation and testing procedures. To this end and within the framework of the European Project Micro2DNA, we work towards exploiting surface stress changes and subsequent bending of microelectromechanical structures combined with capacitive detection. A first sensor employing capacitive detection and silicon micromachined membranes has been developed. The sensor accommodates in a single chip a capacitive DNA sensor array of 256 elements. Each sensor in the array consists of a single crystal silicon membrane that is covered with receptor DNA after surface functionalization and deflects upon exertion of surface stress hybridization. Membrane deflection is detected as a change in device capacitance.

Testing of the sensors is performed in a special setup that allows for the concurrent measurement of multiple sensors in real-time during biological interactions. The setup uses a hybridization chamber designed by CEA-LETI and a custom switch matrix array. To date, operation of the capacitive biosensor array has been tested by monitoring the biotin – streptavidin interaction. The latter is detected as a clear step increase of the biotin functionalized sensor capacitance, while unfuctionalized reference sensors remain stable. In these experiments, unspecifically bound streptavidin is removed during washing at the end of the interaction, as evidenced by the drop in sensor capacitance during washing.





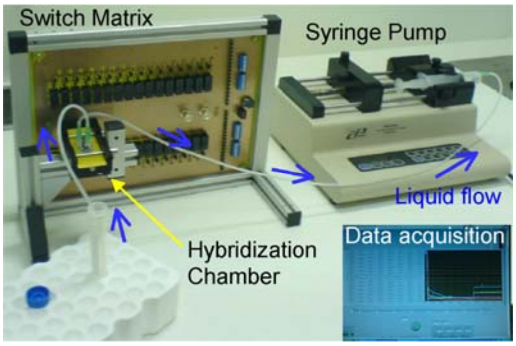


Fig. III.2.11: *Top-left: 16x16 sensor array before Al deposition and functionalization. Bottom: Measurement set-up. Liquids are pumped out of the reservoir and then through the hybridization chamber to end up in the syringe. Top-right: Typical change in capacitance of biotin-functionalized and unfunctionalized (reference) sensors.*

Furthermore, a dedicated ASIC has been designed, using 0.35um CMOS technology, and fabricated at AustriaMicrosytems. The interface is designed around a relaxation oscillator and produces a square wave with frequency which is dependent on the value of the sensor capacitance being read. Additional circuitry allows for trimming of the output according to the sensor capacitance and sensitivity. Moreover the interface is able to read the whole array of 256 capacitive sensing elements by using a 16 x 16 addressing mode to select the sensor to be measured. In a next step the sensor and the ASIC chips will be connected together to allow easy readout of the array.

PROJECT OUTPUT in 2007

Publications in International Journals

1. "Impact of structural parameters on the performance of silicon micromachined capacitive pressure sensors", V. Tsouti, G. Bikakis, S. Chatzandroulis, D. Goustouridis, P. Normand, D. Tsoukalas, Sensors and Actuators A: Physical 137 (1), 20-24, 2007.
2. "Humidity effects in spin-coated films of polythiophene-polystyrene blends" J.Jaczewska, A.Budkowski, A.Bernasik, I.Raptis, J.Raczkowska, D.Goustouridis, J.Rysz, M.Sanopoulou J. Appl. Polym. Sci. 105 67(2007)
3. "Fabrication of conductometric chemical sensors with a novel lithographic method" N.Andreadis, S.Chatzandroulis, D.Goustouridis, K.Beltsios, I.Raptis Microelectron. Eng. 84 1211(2007)
4. "Composite Chemical Sensors Based on Carbon-Filled, Patterned Negative Resists" S.Chatzandroulis, N.Andreadis, D.Goustouridis, L.Quercia, I.Raptis, K.Beltsios Jpn. J. Appl. Phys. B 46 6423(2007)
5. "Enhancement of sensing properties of thin poly(methyl methacrylate) films by VUV surface modification" I.Raptis, J.Kovač, M.Chatzichristidi, E.Sarantopoulou, Z.Kollia, S.Kobe, A.C.Cefalas J. Laser Micro/Nanoengineering 2 200(2007)
6. "Sequential polymer lithography for chemical sensor arrays" M.Kitsara, K.Beltsios, D.Goustouridis, S.Chatzandroulis, I.Raptis Eur. Polymer J. 43 4602(2007)
7. "Single chip interdigitated electrode capacitive chemical sensor arrays" M.Kitsara, D.Goustouridis, S.Chatzandroulis, M.Chatzichristidi, I.Raptis, Th.Ganetsos, R.Igreja, C.J.Dias Sens. Act. B. 127 186(2007)
8. "Swelling of poly(3-alkylthiophene) films exposed to solvent vapours and humidity: Evaluation of solubility parameters" J.Jaczewska, I.Raptis, A.Budkowski, D.Goustouridis, J.Raczkowska, M.Sanopoulou, E.Pamuła, A. Bernasik, J.Rysz, Synth. Met. 157 726(2007)
9. "Disposable bismuth-sputtered electrodes for the determination of trace metals by anodic stripping voltammetry" Ch.Kokkinos, A.Economou, I.Raptis, Th.Speliotis C.E.Efstathiou Electrochem. Commun. 9 2795(2007)
10. "Field-effect transistors with thin ZnO as active layer for gas sensor applications", F. V. Farmakis, A. Speliotis, K. P. Alexandrou, C. Tsamis, M. Kompitsas, I. Fasaki, P. Jedrasik, G. Petersson, B. Nilsson, To appear in Microelecronics Engineering
11. "Nanostructured Oxides on Porous Silicon Microhotplates for NH3 Sensing", R. Triantafyllopoulou, X. Illa, O. Casals, C. Tsamis, A. Romano-Rodriguez, J.R. Morante, To appear in Microelecronics Engineering

Publications in International Conference Proceedings

1. "Wireless Measurement System For Capacitive Pressure Sensors Using Strain Compensated SiGeB", K. Arshak, E. Jafe, T. McGloughlin, T. Corbett, S. Chatzandroulis, D. Goustouridis, IEEE SENSORS 2007 Conference Proceedings, p.4, Atlanta, Georgia, USA, October 28-31, 2007.
2. "Development of Wireless Pressure Measurement System for Short Range medical Applications", K. Arshak, E. Jafer, T. McGloughlin, T. Corbett, S. Chatzandroulis, D. Goustouridis, D.Tsoukalas, P.Normand, O. Korostynska, 30th International Spring Seminar on Electronics Technology, ISSE 2007, pp. 94–99, May 9-13, 2007.
3. "Thermal characterization of Porous Silicon micro-hotplates using IR thermometry", R. Triantafyllopoulou, C. Tsamis, S. Chatzandroulis , T. Speliotis, J. Parthenios, K. Papagelis and C. Galiotis, Solid-State Sensors, Actuators and Microsystems Conference Proceedings,, TRANSDUCERS 2007. International, p. 2271-2274, DOI: 10.1109/SENSOR.2007.4300622

Conference Presentations

1. "Design and fabrication of a micromechanical capacitive DNA sensor array", V.Tsouti, S.Chatzandroulis, D.Goustouridis, P.Normand, D.Tsoukalas, 33th International Conference on Micro- and Nano-Engineering, MNE 2007, Copenhagen, Denmark, September 23-26, 2007.
2. "Direct laser printing of biomolecules on capacitive sensors", C. Boutopoulos, P. Andreakou, S. Chantzandroulis, D. Goustouridis, I. Zergioti, D. Kafetzopoulos, D. Tsoukalas, 3rd International Conference on Micro-Nanoelectronics, Nanotechnology & MEMS, Athens, Greece, November 18-21, 2007.
3. "Direct laser printing of biomolecules on capacitive sensors", I. Zergioti, C. Boutopoulos, P. Andreakou; C. Chatzandroulis, D. Goustouridis, D. Tsoukalas, , 9th International Conference on Laser Ablation, COLA 2007, Tenerife, Spain, September 24-28, 2007.
4. "Thermal characterization of Porous Silicon micro-hotplates using IR thermometry", R. Triantafyllopoulou, C. Tsamis, S. Chatzandroulis , T. Speliotis, J. Parthenios, K. Papagelis and C. Galiotis, TRANSDUCERS'07/ EUROSENSORS XXI, June 10-14 2007, Lyon, France, (Poster)
5. "Detection of CO and NO using low power Metal Oxide sensors", R. Triantafyllopoulou & C. Tsamis, Third Conference on Microelectronics, Microsystems, Nanotechnology, MMN 2007, 18-21 November 2007, Athens, Greece (Poster)
6. "Field-effect transistors with thin ZnO as active layer for gas sensor applications", F. V. Farmakis, A. Speliotis, K. P. Alexandrou, C. Tsamis, M. Kompitsas, I. Fasaki, P. Jedrasik, G. Petersson, B. Nilsson, Micro- and Nano-Engineering, MNE 2007, 23-26 September 2007, Copenhagen, Denmark (Poster)

7. “Nanostructured Oxides on Porous Silicon Microhotplates for NH3 Sensing”, R. Triantafyllopoulou, X. Illa, O. Casals, C. Tsamis, A. Romano-Rodriguez, J.R. Morante, Micro- and Nano-Engineering, MNE 2007, 23-26 September 2007, Copenhagen, Denmark (Poster)
8. “Electrical characterization of field-effect zinc oxide transistors for gas sensing applications”, F.V.Farmakis, P.Jedrasik, C.Tsamis, M.Kompitsas, I.Fasaki, A.Speliotis, IMA 2007, 30 September – 04 October 2007, Rio-Patras, Greece (Oral)