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:

EU - IST-FP6-STREP-027333 Micro2DNA, "Integrated polymer-based micro fluidic micro system for DNA extraction, amplification, and silicon-based detection", P. Normand
Hellenic National Strategic Reference Framework (ESPA) 2007-2013, Contract no. MICRO2- ΣΕ-Γ, S. Chatzandroulis

Main Activities in 2010:

In 2010, 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. FET-type chemical sensors*

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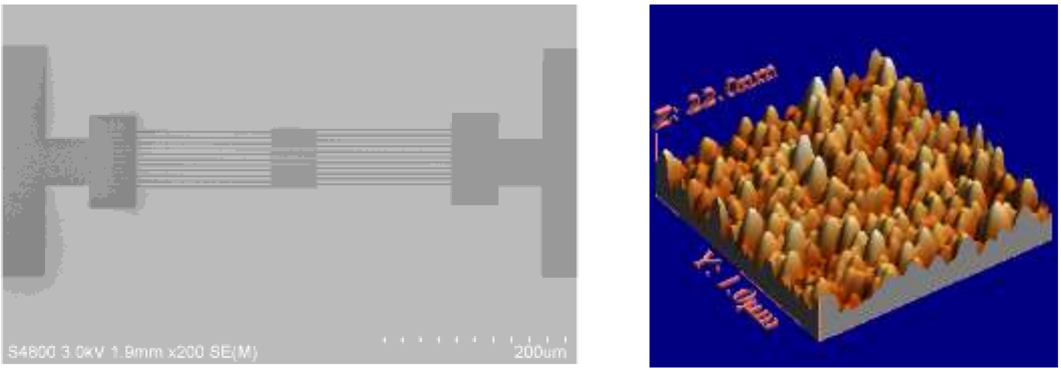
Chemical sensors for wireless applications are of major interest since they turn into reality the possibility to sense and monitor environmental changes in hard-accessible mediums or even to escort environment-sensitive products in order to monitor and build environment-related database. Low-energy consumption, low or 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.

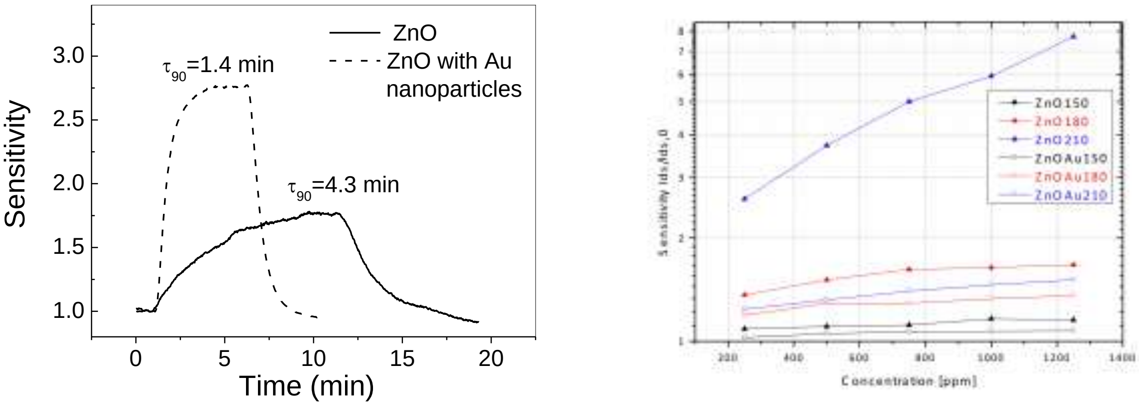
During this year, we continued our efforts on the fabrication of interdigitated bottom-gate FET devices with various channel lengths (from 0.3 μm to 2 μm) (Figure 1a). On the top of the interdigitated electrodes, a 50-nm-thick zinc oxide layer was grown by Pulsed Laser Deposition, as the active layer. Alternatively, Au-nanoparticles were also deposited on top of ZnO with the PLD technique in order to investigate the influence of Au on ZnO. Figure 1b shows an AFM image of as-deposited thin ZnO film grown on oxidized silicon wafer. The average grain size of around 80 nm is slightly affected by the annealing process due to the low (400^{O}C) temperature used. The indicated high surface-to-volume ratio favors the application of such films as gas sensors since the chemical active area is enhanced.



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

Fig. 1: *(a) SEM images showing the interdigitated source and drain electrodes of the bottom gate FET device. (b) AFM image picture of as-deposited thin ZnO film grown on oxidized silicon wafer. The average grain size of around 80 nm is not affected by the annealing process due to the low (400^O C) temperature used.*

Figure 2a shows a comparison in CO sensing between a ZnO gas sensor without Au and with Au nanoparticles. It has to be noted that both sensors were held at 200^{o}C during the experiments and that the CO was introduced with dry air. It is easily observed that the sensitivity is more than 1.5 times higher for the sensor with the Au nanoparticles. In addition, the response time t_{90} (t_{90} is defined as the time needed for the signal to achieve the 90% of its final value) is 3 times shorter for the ZnO/Au nanoparticles gas sensor. Figure 2b shows the Sensor sensitivity as a NH_3 concentration for ZnO sensors with and without gold nanoparticles for temperatures ranging from 150-210^{o}C.. We observe that depending on the measurement temperature the introduction of Au significantly alters sensitivity in NH3



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

Fig. 2: *(a) Sensitivity vs time for ZnO sensors with and without gold nanoparticles. The measurements were performed at 200^{o}C. (b) Sensor sensitivity as a NH_3 concentration for ZnO sensors with and without gold nanoparticles for temperatures ranging from 150-210^{o}C.*

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B: Polymer based chemical sensor arrays

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Sorption of VOCs and moisture in thin supported polymer films are important phenomena to a variety of applications, such as coatings, microelectronics manufacturing and chemical sensors. A relatively simple methodology based on White Light Reflectance Spectroscopy is applied to monitor vapor – induced thickness changes of polymer films, supported on suitable silicon substrates. The methodology developed is very useful for the selection of sensing materials in all sensing principles where polymer is used e.g. chemcapacitors, chemresistors, cantilevers, QCM.

The measured equilibrium thickness expansion of various polymers (methacrylic, siloxane, …), exposed to different activities (α_s) of water, methanol, ethanol and ethyl acetate vapor, is used to determine the sorption isotherm of each system, assuming unidirectional swelling due to the constraining rigid support.

The deduced sorption isotherms were fitted to the Flory- Huggins equation, by non-linear regression analysis, and interaction parameters χ were determined for each binary system. As an example, the moisture sorption data of all polymers are presented in Fig. 3. The relative sorption capacity of the different classes of polymers towards the four vapors is in line with the expected solubility interactions between solvent and solute. Furthermore, an estimate of the solubility coefficient S, at the limit of infinite dilution, expressed as $S= \varphi_S / a_s = \exp(-1-\chi)$, is made. The correlation of the values of S to the differences of the Hansen solubility parameters Δδ between solute and polymer of each binary system (Fig. 4) exhibits a sharp decay of solubility coefficient with increasing Δδ. The results indicate that the applied optical methodology is suitable for screening polymeric materials for specific applications, on the basis of their sorption properties.

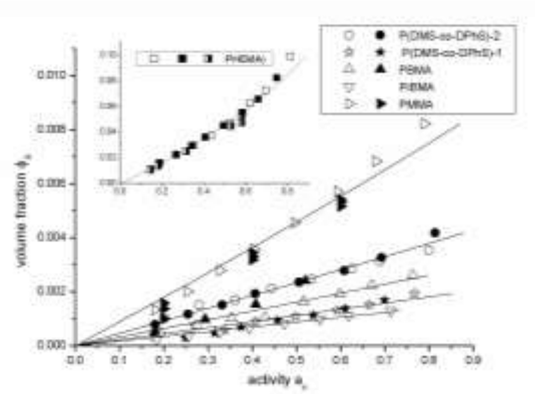

Fig. 3: *Sorption isotherms of H_2O vapor in polymer films of thicknesses L_o =197-737nm, at 30 ^{0}C (points). Lines represent fitting to the Flory- Huggins equation with interaction parameter χ: 1.58 (PHEMA); 3.73 (PMMA); 4.39 [P(DMS-co-DPhS)-2]; 4.75 (PBMA); 5.11 [P(DMS-co-DPhS)-1];5.36 (PiBMA)*

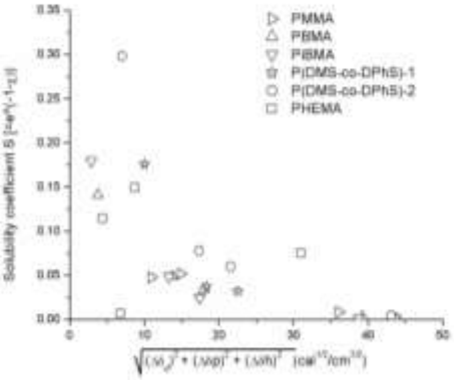

Fig. 4: *Correlation of solubility coefficients S with three-dimensional solubility parameter differences*

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C. Capacitive Type Sensors*

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Capacitive DNA Sensors Arrays

The detection of DNA hybridization using ultrathin Si membrane capacitive micromechanical biosensor organized in a 16 x1 6 array has been studied. The biosensor exploits the ability of the ultrathin membrane to deflect upon surface stress variations caused by biological interactions. Probe DNA molecules are immobilized on the membrane surface and the surface stress variations during hybridization with their complementary strands force the membrane to deflect and effectively change the capacitance between the flexible membrane and the fixed substrate. The sensor array comprises 256 such sensing sites thus allowing the concurrent sensing of multiple DNA mutations. The biosensor and its performance for the detection of complementary DNA strands are demonstrated using beta-thalassemia oligonucleotides. The experimental results show that the sensors are able to detect DNA hybridization using 9nM sample and to discriminate single nucleotide mismatches.

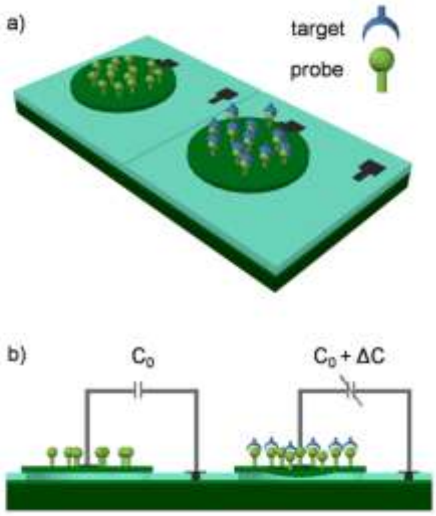

Fig. 5: *Schematic of the capacitive sensing elements. The surface stress variations induced during the biomolecular interactions change the capacitance between the ultrathin Si membranes and the fixed substrate.*

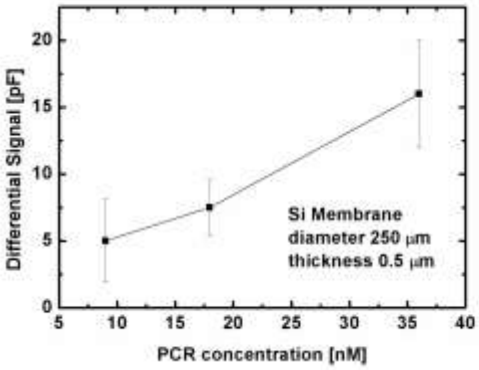

Fig. 6: *Average differential response (average CD19N minus average CD19M sensors) of biosensor arrays with sensing elements of 0.5μm Si membrane thickness and 250μm diameter for three different PCR concentrations. The errors are estimated by the variations among the sensing elements in the same array.*

Electronic Readout for Capacitive Sensor Arrays.

An electronic readout system for multiple capacitive sensors was designed and manufactured as an ASIC. The output signal of the readout is a square wave, with the oscillation period being linearly modulated by the sensor capacitance. The system focuses on the simplicity of the design, while integrating basic peripheral components on-chip. Components such as charge/discharge current control unit, a multiplexing unit and a bandgap voltage reference are embedded, to obtain a stable and linear readout system for multiple sensors of variable types and capacitance ranges. The ASIC is hosted on a PCB with a supervising microcontroller, which is programmed to produce ratiometric measurements using reference capacitances to minimize parasitic effects, returning the results over a USB interface to a personal computer. The ASIC was designed and fabricated in AMS 0.35um CMOS technology, and was tested using capacitive pressure sensors, exhibiting up to 0.89 μs/pF sensitivity.

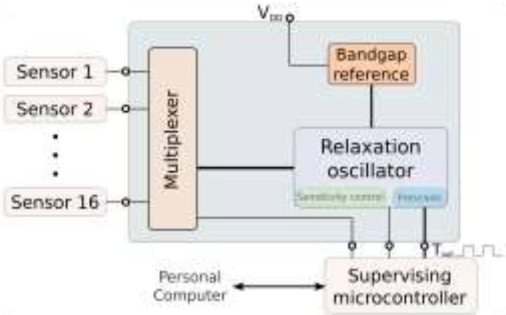

Fig. 7: *System block diagram*

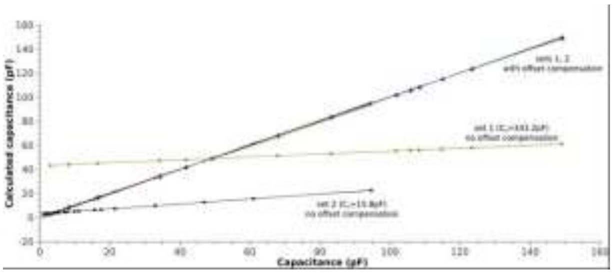

Fig. 8: *Calculated capacitances with and without offset compensation, for two sets of measurements*

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PROJECT OUTPUT IN 2010

Publications in International Journals

1. “Vapor-induced swelling of supported methacrylic and siloxane polymer films: determination of interaction parameters” Manoli K, Goustouridis D, Raptis I, Valamontes E, Sanopoulou M, J. Appl. Polym. Sci. 116 184-189 (2010)
2. “Determination of Trace Tl(I) by Anodic Stripping Voltammetry on Novel Disposable Microfabricated

Bismuth-Film Sensors" Kokkinos Ch, Economou A, Raptis I, Speliotis Th, Electroanalysis 22 2359-2365 (2010).

3. "Polymer based chemical sensor array fabricated with conventional microelectronic processes" Kitsara M, Goustouridis D, Valamontes E, Oikonomou P, Beltsios K, Raptis I, J. Optoelectron. Adv. Mater. 12 1147-1151 (2010).
4. V. Tsouti, C. Boutopoulos, D. Goustouridis, I. Zergioti, P. Normand, D. Tsoukalas, S. Chatzandroulis, "A chemical sensor microarray realized by laser printing of polymers*", Sens. Act. B: Chemical*, vol. 150 (1), pp. 148-153 (2010).
5. V. Tsouti, C. Boutopoulos, P. Andreakou, M. Ioannou, I. Zergioti, D. Goustouridis, D. Kafetzopoulos, D. Tsoukalas, P. Normand, S. Chatzandroulis, "Detection of DNA mutations using a capacitive micro-membrane array", *Biosensors and Bioelectronics*, vol. 26 (4), pp. 1588-1592 (2010).
6. M. Kandyla, S. Chatzandroulis, I. Zergioti, "Laser induced forward transfer of conducting polymers", (2010) *Opto-Electronics Review*, vol 18 (4), pp. 345-351
7. S. Chatzandroulis, V. Tsouti, M. Ioannou, C. Boutopoulos, I. Zergioti, D. Goustouridis, J. Hue, R. Rousier, D. Tsoukalas, P. Normand, and D. Kafetzopoulos, «Sensitivity Investigations Of Surface Stress Capacitive DNA Sensor», 9th Annual IEEE Conference on Sensors IEEE Sensors 2010 Conference, November 1-4, 2010

Publications in International Conference Proceedings

1. "Micro-fabricated cell-on-a-chip devices with integrated metal-film electrodes for trace metal analysis by stripping voltammetry" Kokkinos Ch, Economou A, Raptis I, Speliotis A, Micro & Nano Engineering 2010 (Genoa, Italy, 09/2010)
2. I. Ramfos, I., Chatzandroulis, S., "A 16-channel capacitance-to-period converter with offset compensation for sensor applications", Electronics, Circuits, and Systems (ICECS), 2010 17th IEEE International Conference on

Conference Presentations

1. "Characterization of the vapor sorption properties of methacrylic and siloxane polymers by an optical method" Manoli K, Oikonomou P, Goustouridis D, Raptis I, Sanopoulou M, 8th Hellenic Polymer Soc. Symp. (Crete, Greece, 10/2010)
2. "Influence of Au nanoparticles on ZnO field-effect transistors fabricated by Pulsed Laser Deposition", F.V. Farmakis, N. Kelaidis, C. Chatzimanolis-Moustakas, E. Makarona, C. Tsamis, M. Kompitsas, I. Fasaki, Th. Speliotis and P. Jedrasik, E-MRS Spring Meeting 2010, Symposium R: Laser Processing and Diagnostics for Micro- and Nano-applications, 7-11 June 2010, Strasburg, France

Msc Thesis

M.Fillipidou, «Study of Biological Interactions using Si micromechanical sensors»