PROJECT III.1A
MECHANICAL AND CHEMICAL SENSORS

Permanent Researchers: S. Chatzandroulis, I. Raptis

Post Doctoral Scientists: P. Oikonomou, A. Olzierski

MSc Students: M.-I. Georgaki

Other staff under contract (technical personnel): A. Botsialas

External Collaborators: M. Sanopoulou (Physical Chemistry Depart./IAMPPNM/NCSR Demokritos), D. Goustouridis (TEI of Piraeus), M. Chatzichristidi (Univ. Athens), D. Dimou, S. Katsikas (Prisma Electronics S.A.)

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 based sensors
- Realization of sensors for specific industrial applications with emphasis on medical, food and automotive fields

FUNDING

ALEPOU "Autonomous and integrated system for in-situ and continuous contaminant gases monitoring in industrial environments" Funded by General Secretariat for Research & Technology – 19SMEs2010

MAIN ACTIVITIES in 2012

In 2012 our main activities were focused on the following tasks:

A. Polymer based chemocapacitor arrays
B. Zero-Power colorimetric humidity sensors
C. Capacitive Type Sensors

A. Polymer based chemocapacitor arrays

P. Oikonomou[1], A, Botsialas[1], I. Raptis[1], M. Sanopoulou[2]
[1]Department of Microelectronics, IAMPPNM, NCSR 'Demokritos'
[2]Department of Physical Chemistry, IAMPPNM, NCSR 'Demokritos'

In the research field of gas sensors there is an increasing need for low cost and low power consumption devices that are capable of measuring the temperature, the humidity and the gaseous composition of the ambient atmosphere. For this purpose, complete systems are needed where the sensor array, the read-out electronics and the power supply are integrated in the same miniaturized module. A hybrid gas sensing module consisting of (a) 8-polymer coated capacitive sensor array and (b) low power control and read-out electronics was developed, fig 1 and fig 2, aiming at the detection of volatile organic compounds in air.

In chemocapacitors, the swelling of the polymeric film that is induced by sorption of analyte molecules causes a change of the effective dielectric constant of the polymeric layer and thus an increase of the capacitance of the device. In order to improve the sensing performance of the device a software tool aiming at the prediction of chemocapacitor response was introduced. It is based on experimental determination of the swelling ability of polymeric sensing materials due to the sorption of analytes-extracted data by swelling measurements based on White Light Reflectance Spectroscopy (WLRS)-in conjunction with finite element electromagnetic modeling for the InterDigitated Electrode (IDE) capacitor. The methodology was tested against experimental capacitance measurements in different polymer–vapor analyte systems with very promising results. A typical example of the responses of several polymer coated sensors of the sensor array upon exposure to tetrahydrofuran (THF) vapors in conjunction with the simulated responses according to the applied proposed methodology is illustrated in fig. 3, implying a feasible calculation of the capacitance value of any IDE layout when it is coated with the polymer of interest and also when this polymer-coated IDE is exposed to different vapor concentrations of the target-analyte.

Furthermore, temperature effects has been recently evaluated as of critical importance for accurate measurement in real environments and several approaches have been suggested in order to either remove this effect by operating the device at constant temperature or by accurate recording of the temperature during operation of the sensor and compensating for temperature variations. Accurate recording of temperature concurrently to the capacitance signal of the sensors enabled the construction of a temperature (ΔT)-capacitance (ΔC) calibration curve for each sensor. The linear ΔC–ΔT relations were found to depend on the specific polymeric sensing layer, and were then used to demonstrate the importance of the said correction, in Volatile Organic Compounds (VOCs) sensing in humid environment and under relatively unstable temperature conditions. By subtracting the interfering signal of temperature change we can ensuree that the sensors capacitance response upon exposure to certain analyte or mixture of analytes is a result of the sorption capacity of the polymer-coated sensor and not due to temperature variations, fig. 4. This way the sensor array can be used for applications in real environments where the operation temperature is unstable.

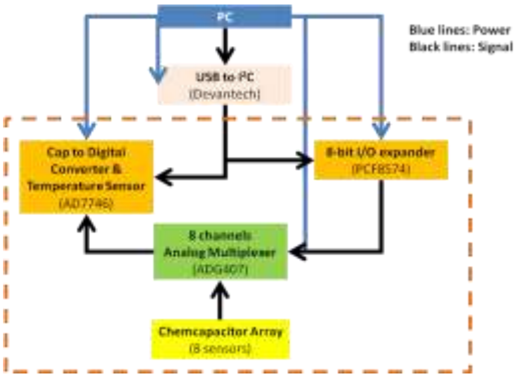


Fig. 1. *Block diagram of the gas sensing module and electronic interface with the PC for the data acquisition and data processing. For wireless data transmission, the USB to I^2C chip will be replaced by a wireless module.*

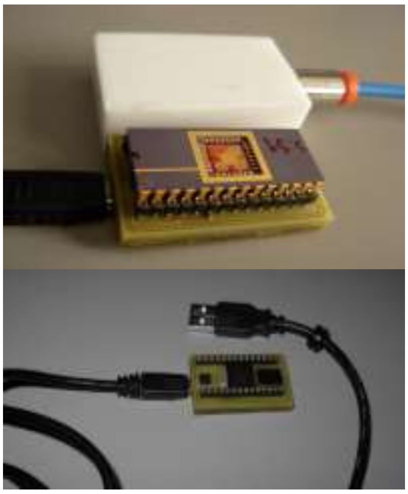
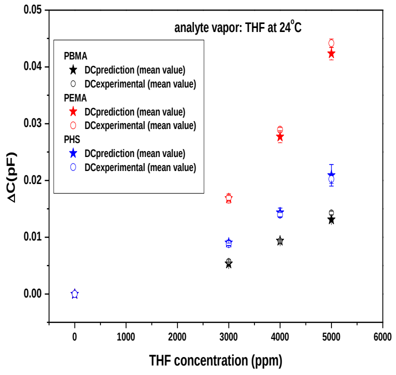


Fig. 2. *Photos from the gas sensing module: (top image) 8-sensor array and electronics and chamber, (bottom image) the read-out and control electronics sub-module.*



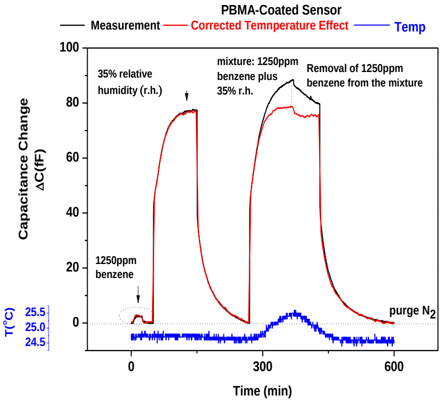


Fig. 3. *Capacitance change of chemocapacitors coated with PBMA, PEMA and PHS layers upon sorption of THF as measured (open points) and as calculated from the modelling approach based on polymer swelling (filled points). The error bars represent standard deviation derived from at least three samples. The agreement between the modelling and the experimental results is very good.*

Fig. 4. *Dynamic response of a PBMA-coated sensor to controlled concentrations of water, benzene vapor and their mixture. The temperature is measured with the embedded to the capacitance converter temperature sensor.*

**For more information please contact Dr. I. Raptis (e-mail:*raptis@imel.demokritos.gr*)*

B. Zero-Power colorimetric humidity sensors

M.-I. Georgaki, P. Argitis, N. Papanicolaou[1], I. Raptis[1], M. Chatzichristidi[2]
[1]Department of Microelectronics, IAMPPNM, NCSR 'Demokritos'
[2]Department of Chemistry, University of Athens

One-Dimension Photonic Crystals (1-D PC) is a multilayer stack of two alternating transparent materials with different refractive indices. Such 1-D PC acts as Bragg mirror, fig. 1, and upon illumination with broad-band light a particular reflectance spectrum with narrow-band and high reflectance spectral region is observed whereas all other wavelengths are highly transmitted through the multilayer stack. The optical properties of the 1-D PC depend on film thicknesses, layers' refractive indices etc.

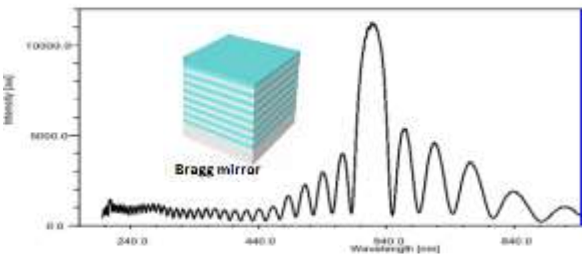


Fig. 1. *Theoretical reflectance spectrum from a Bragg mirror. On the left side a schematically representation of an eight bilayer stack is depicted.*

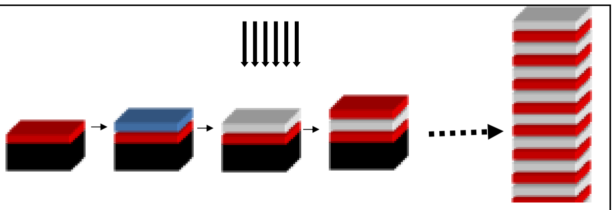


Fig. 2. *Process flow chart for the fabrication of the 1-D polymeric photonic crystal. The PHEMA layers are spin coated and Post Apply Baked while the EPR layers are processed as chemically amplified resists: spin coated, Post Apply Baked, uniformly exposed at DUV and Post Exposure Baked*

A novel 1-D polymeric photonic crystal was designed, fabricated and evaluated as a humidity sensor. The polymeric photonic crystal is consisted of a multilayer stack of sequential hydrophilic (PHEMA: Poly Hydroxy Ethyl MethAcrylate) and hydrophobic (EPR: epoxy based negative tone resist) layers applied using conventional photolithographic steps: spin-coating and DUV exposure, fig. 2. These two polymeric materials are dissolved at different casting solvents which is a prerequisite for the successful deposition of the related layers. The polymeric PCs were evaluated through dissolution experiments and SIMS measurements revealing very well defined interfaces between the hydrophilic and hydrophobic layers.

During exposure in a humidity environment, the hydrophilic layers of the sensor swell, hence growing its optical path and giving a red-shift of the reflectance peak and consequently a different colour of the device. The colorimetric humidity sensor does not require external power since its sensing ability is based on the reflectance peak shift of the photonic crystal in the visible spectrum (colour change of the sensor).

The reflectance spectra at equilibrium from 0 to 90%RH are illustrated in fig. 3 showing a linear red-shift of the reflectance peak by 62nm. In order to enhance the spectral shift due to humidity the PHEMA film thickness should increase whereas the EPR decrease in order to keep the reflectance peak shift in the visible range. By considering 40nm as the lower thickness limit for reliable and reproducible application through spin-coating of high quality polymeric film, PHEMA film thickness should be 140nm. In fig. 4 the reflectance peak shift for various combinations of PHEMA-Cross-EPR film thickness is illustrated. Film thicknesses have been carefully selected in order that the reflectance peak at nitrogen to be nearly the same for all cases. Clearly the increase of PHEMA film thickness provide of larger reflectance peak shift for the same humidity change.

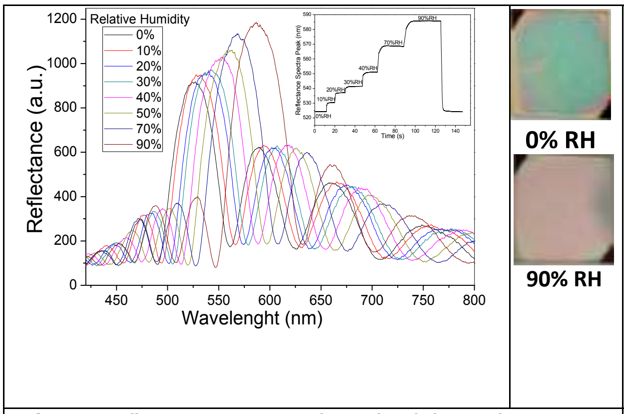


Fig. 3. Reflectance spectra (raw data) for various humidity concentrations. Increase of humidity level in the environment causes swelling of hydrophilic PHEMA and thus red-shift of the reflectance peak.

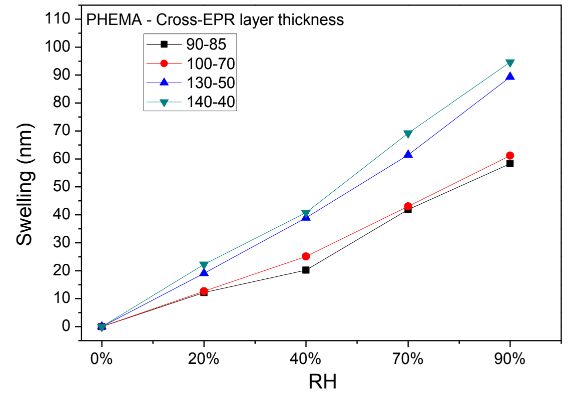


Fig. 4. Effect of layer thickness of both PHEMA and cross-EPR for various combinations aiming at similar wavelength of the reflectance peak (λo) at dry environment. The increased layer thickness of the hydrophilic material causes enhanced responses in terms of shift per humidity change. In all cases the spectral shift is linear in respect to the humidity level revealing a linear swelling of PHEMA layers.

**For more information please contact Dr. I. Raptis (e-mail:*raptis@imel.demokritos.gr*)*

C. Capacitive Type Sensors*

S. Chatzandroulis, V. Tsouti, I. Ramfos, P. Broutas, I. Zergioti[1], D. Tsoukalas[1], G.Tsekenis[2], P. Normand
[1]National Technical University of Athens,
[2]Foundation of Biomedical Research, Academy of Athens, Greece

Micromechanical Capacitive DNA Sensor Arrays

A micromechanical capacitive biosensor array has been developed using a novel fabrication process. Each biosensor in the array consists of a flexible membrane and a fixed electrode implemented on the substrate. Probe molecules are immobilized on the membrane surface and the surface stress variations during biological interactions force the membrane to deflect and effectively change the capacitance between the flexible membrane and the fixed substrate. The array consists of 60 sensors and thus is suitable for parallel sensing. The process is characterized by the self-alignment of the sensitive flexible membranes and the use of silicon fusion bonding to fabricate the complete device.

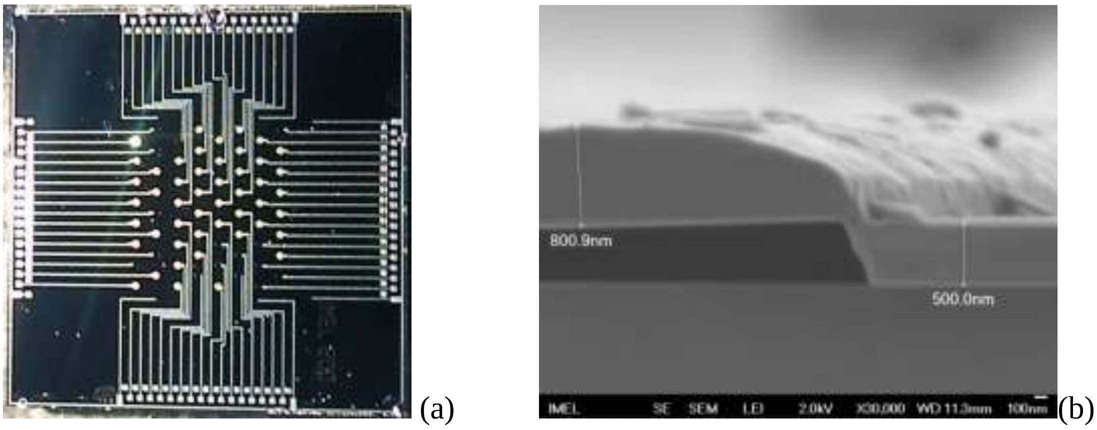


Fig. 1. (a) Microphotograph of a fully processed biosensor array and (b) SEM view of the circular membranes.

The array performance was tested using the K-ras gene which is linked to colon cancer. In these tests, alleles of the gene (Wild Type και Mutant) were printed and immobilized on sensor array membranes using Laser Induced Forward Transfer (LIFT) at NTUA (Figure 2). The tests were performed in a flow cell into which a test sample of mutated K-ras is inserted after a first wash with a buffer solution. To enable the concurrent measurement of multiple biosensors in the array a switch relay matrix is used to select the sensing element to be read using an HP4278A capacitance meter. Control of the whole system is performed via a Labview program running on a PC. First experimental results indicate that the sensors were able to detect the interaction between the mutant probes and the mutated part of the K-ras gene (red line in Figure 3). In the same graph, the response of a sensor on which the wild type probe was immobilized and subsequently did not interact with the mutated part of the K-ras gene is depicted (blue line), as well as the response of a simple Al capacitor (with no deflectable electrode) on which mutated probes were immobilized (magenta line in Figure 3 3).

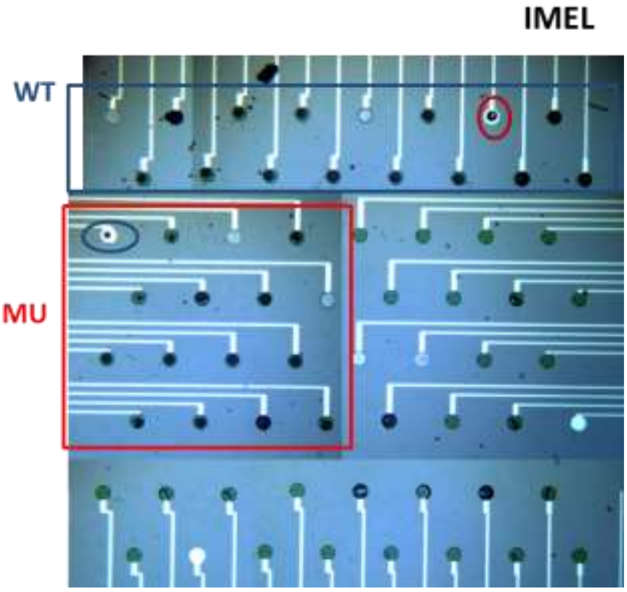


Fig. 2. *Capacitive biosensor array onto which K-ras probes (20 μM) were printed and immobilized. The array hosts Si membranes 1.34μm thick with 200μm diameter.*

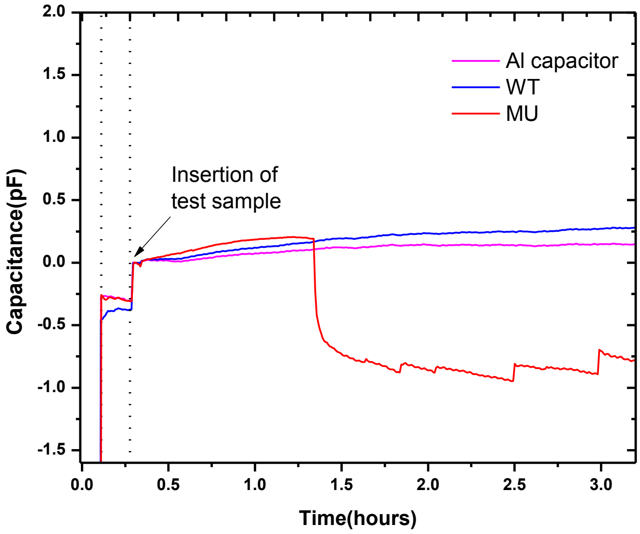


Fig. 3. *Response of sensing elements in the sensor array to mutated (MU) K-ras genes (100 ng/μl). The test sample is inserted at around 18 min (~0.3h). Only the biosensor with the immobilized mutant probes changes its capacitance (~ 1pF) whereas the biosensor with the immobilized WT probes as well as the Al capacitor remain stable after the sample insertion.*

PROJECT OUTPUT in 2012

Publications in International Refereed Journals

1. *Microfabricated disposable lab-on-a-chip sensors with integrated bismuth microelectrode arrays for voltammetric determination of trace metals,*
   Ch.Kokkinos, A.Economou, I.Raptis
   Anal. Chem. Acta 710 1(2012)
2. *Polymer-BaTiO3 Composites: Dielectric constant and vapour sensing properties in chemcapacitor applications,*
   K.Manoli, P.Oikonomou, E.Valamontes, I.Raptis, M.Sanopoulou
   J. Appl. Polym. Sci. 125 2577(2012)
3. *Compensation of Temperature Variations in Chemcapacitive Gas Sensing Systems,*
   P.Oikonomou, A.Botsialas, D.Goustouridis, E.Valamontes, M.Sanopoulou, I.Raptis
   Sensor Lett. 10 736(2012)
4. *Chemocapacitor performance modeling by means of polymer swelling optical measurements,*
   P.Oikonomou, A.Botsialas, K.Manoli, D.Goustouridis, E.Valamontes, M.Sanopoulou, I.Raptis, G.P.Patsis
   Sens. Act. B 171-172 409(2012)
5. *Sensitivity Study of Surface Stress Biosensors Based on Ultra-thin Si Membranes,*
   V.Tsouti & S.Chatzandroulis
   Microelectronic Engineering, vol. 90, pp. 29-32 (2012)
6. *Evaluation of Capacitive Surface Stress BioSensors,*
   V.Tsouti, C.Boutopoulos, M.Ioannou, D.Goustouridis, D.Kafetzopoulos, I.Zergioti, D.Tsoukalas, P.Normand, S.Chatzandroulis
   Microelectronic Engineering, vol. 90, pp. 37-39 (2012)
7. *Capacitive Microsystems for Biological Sensing,*
   V. Tsouti, C. Boutopoulos, I. Zergioti, S. Chatzandroulis
   Biosensors and Bioelectronics, vol. 27 (1), pp. 1-11 (2011)
8. *A 16-channel capacitance-to-period converter for capacitive sensor applications,*
   Ramfos, S. Chatzandroulis
   Analog Integrated Circuits & Signal Processing Analog Integrated Circuits and Signal Processing, June 2012, Vol. 71, issue 3, pp 383-389, DOI: 10.1007/s10470-011-9738-y
9. *Self-Aligned Process for the Development of Surface Stress Capacitive Biosensor Arrays,*
   V. Tsouti, M.K. Filippidou, C. Boutopoulos, P. Broutas, I. Zergioti, S. Chatzandroulis
   Sens. Act. B , Vol. 166–167, pp. 815-818 (2012)
10. *Surface functionalization studies and direct laser printing of oligonucleotides towards the fabrication of a micromembrane DNA capacitive biosensor,*
    G. Tsekenis, M. Chatzipetrou, J. Tanner, S. Chatzandroulis, D. Thanos, D. Tsoukalas, I. Zergioti
    Sens. Act. B, vol. 175, pp. 123–131 (2012)

Published Conference Proceedings

1. *Real time detection of volatile organic compounds through a chemocapacitor system,*
   E.Valamontes, G.Patsis, D.Goustouridis, P.Oikonomou, A.Botsialas, I.Raptis, M. Sanopoulou
   IMCS 2012 (Nuremberg, Germany, 05/2012)
2. *Zero-Power humidity sensor based on 1-D photonic crystal colour change,*
   M.-I.Georgaki, A.Botsialas, P.Argitis, M.Chatzichristidi, J.Rysz, A.Budkowski, I.Raptis
   EuroPtrode 2012 (Barcelona, Spain, 04/2012)

Conference Presentations

Fabrication of a capacitive micro-mechanical biosensor array with self-alignment of the ultrathin Si diaphragm and laser printing of bioreceptors,
S. Chatzandroulis, V. Tsouti, G. Tsekenis, M. Chatzipetrou, D. Thanos, I. Zergioti
2012 MRS Spring Meeting & Exhibit, April 9 - April 13, 2012, San Francisco, California

Masters Dissertations completed in 2012

Realization of photonic polymeric multilayers as humidity sensors,
Maria-Isidora Georgaki
MSc Thesis held at IMEL/NCSR Demokritos (Supervisor: I. Raptis)
Defended at the National and Kapodistrian University of Athens, Dept. of Chemistry