Steps Towards Large Mylar Membrane Based Multiple Transducers, Application to Chemical Adsoptions Sensors

Jorel Corentin, Didier Robbes, Matthieu Denoual, Julien Grand, Svetlana Mintova, Loïc Le Marrec

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Jorel Corentin
GREYC
Normandie Univ, UNICAEN, ENSICAEN, CNRS,
Caen, France
corentin.jorel@unicaen.fr

Robbes Didier
GREYC
Normandie Univ, UNICAEN, ENSICAEN, CNRS,
Caen, France
didier.robbes@unicaen.fr

Denoual Matthieu
GREYC
Normandie Univ, UNICAEN, ENSICAEN, CNRS,
Caen, France
matthieu.denoual@ensicaen.fr

Grand Julien
LCS
Normandie Univ, ENSICAEN, UNICAEN, CNRS,
Caen, France
jgrand1985@gmail.com

Mintova Svetlana
LCS
Normandie Univ, ENSICAEN, UNICAEN, CNRS,
Caen, France
mintova@ensicaen.fr

Le Marrec Loïc
IRMAR
UMR 6625, Université de Rennes 1,
Rennes, France
loic.lemarrec@univ-rennes1.fr

***Abstract*—Integrated gas sensors and measuring systems are desired devices in many domains, including large scales applications. One of the main issue still is their poor chemical selectivity despite the very wide diversity of developed systems. In this paper, we present our approach based on selectively adsorbing zeolite thin films. A full instrument has been developed with up to five transduction means based on a single adsorbing layer of zeolite. That layer is suspended on a large Mylar membrane capped with a functionalized Aluminum thin film. We present also an analytical mechanical model that allows estimating the instrument intrinsic possibilities.**

Keywords—Chemical Sensor, Membranes, Zeolite, Single Input - Multiple Output, Mechanical Model

I. Introduction

Chemical adsorption on surfaces, and more specifically in zeolite thin films, has been shown to be chemically selective and is considered a method of choice in the gas sensing state of the art [1]-[3]. Nonetheless, sensors characterization is still difficult, especially if direct comparison is desired. Moreover, adsorption phenomenon are associated to various transduction mechanisms to create the final sensor voltage. Adsorption is directly linked to a mass variation, or, indirectly, to a dielectric susceptibility variation, especially if the adsorbed analyte is made of polarized or highly polarizable molecules. Electrical conductivities or heat capacity variations can also be associated with the adsorption. Once these physical quantities are influenced by adsorption, devices aim to convert the associated variations to output voltage variations, and finally obtain a usable transfer between the analyte concentration and the output voltage.

The aim of that contribution is to present the instrument we developed to make use of these various transduction mechanisms while the analyte adsorption is common, a concept we previously called Single Input - Multi Outputs (SIMO) [4]. In the present work, it is made using microstrips of Aluminum to produce resistive meanders and interdigitated pairs of electrodes working respectively as resistive transducers or capacitive transducers on a Mylar membrane. This work was conducted in the framework of the project C^2-MTM [5], which also included MEMS integration aspects towards miniaturized arrays of sensors to address the Multi Inputs – Multi Output (MIMO) challenges of measuring simultaneously different gas concentration in the same gas vector. This aspect of the work is presented in another paper [6].

After describing the design of the instrument and its multiple outputs part II, the mechanical model of the oscillating membrane is presented in part III.

II. Multiple Outputs Instrument

A. Membrane functionalisation

Fig. 1 show the geometries of the 30 nm thick aluminum meanders. Various tensions (few 100g up to 1 kg) were used to glue the Mylar membranes on an emptied PCB square with thicknesses down to 1.5 µm. Sensing devices like the one pictured in Fig. 1 were fabricated as follows: ion beam sputtering of the gold contacts through a shadow mask, photolithography and wet etching of the aluminum path.

The zeolite film was deposited in the µm range by drop coating. This thickness range was shown to be optimal in terms of filling factor and speed [7]. The zeolite crystals with MFI type framework structure were dispersed in ethanol with

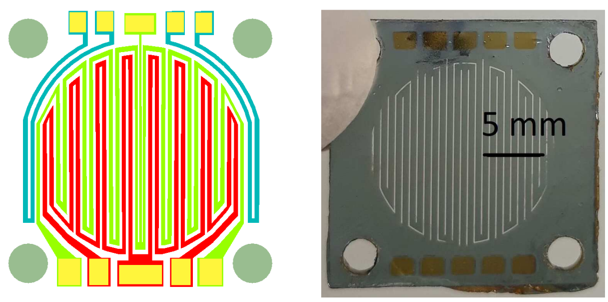

Fig. 1. Left : Functional top view of the aluminum meander. The two intricated meanders (red and green) act as resistive elements when outer contact pads are used, or as an interdigitated capacitance when used through their inner contact pads. The outer blue meander act as a thermistor to evaluate the PCB temperature. Right: Picture of a suspended mylar membrane with 500 um large 40 nm thick Aluminum strip before Zeolite coating

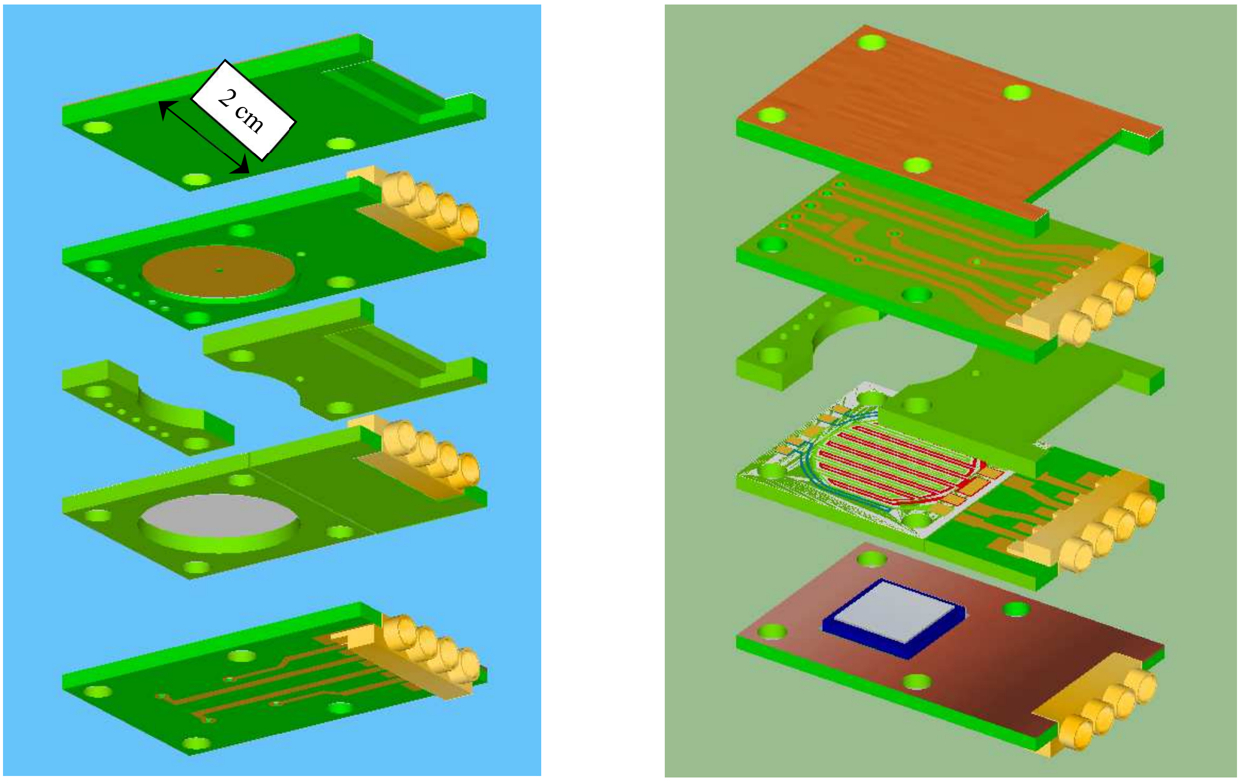

Fig. 2. Expanded sketch of the SIMO device. From bottom to top (1) non contacting amplifier (blue square) to monitor membrane vibrations (capacitive mode), (2) SIMO membrane upon its PCB holder (see Fig. 3), (3) Analysis cell's walls and access, (4) Acoustic excitation, (5) cap.

different solid contents (1 to 10 wt. %) to form homogenous films with controllable thicknesses.

The zeolite films were annealed at 80 °C for 20 minutes after drying in ambient air. The thickness of the zeolite films was varied by changing the concentration of the zeolite crystals in the coating suspension or by renewing the drop coating. Several zeolite films were prepared and thicknesses were monitored by scanning electron microscope (SEM).

B. *Transductions*

The meanders geometry together with the contact pads distribution allow various working modes to link the analyte adsorption to outputs. Those using resistive transduction are:

- One resistive meander to heat and one to measure temperature due to the metallic R(T) behavior, then allowing the calorimetric evaluation of the adsorbed mass [8].
- Direct measure of the resistance change when exposed to the analyte because conductivity is influenced by the adsorption, through strain gauge effect.
- Evaluation of the membrane vibration spectrum under acoustic excitation to reflect mass variation effects, through strain gauge effects in the thin metallic meander.

Those using capacitive transduction means are:

- Capacitance variation of the full interdigitated pair of meanders, allowing dielectric susceptibility evaluation as linked to adsorption,
- Vibration spectrum evaluation under acoustical excitation measured with a capacitance effect: the aluminum meander is biased at a common voltage and a voltage amplifier is positioned just below (~100 µm) to record voltage variations.

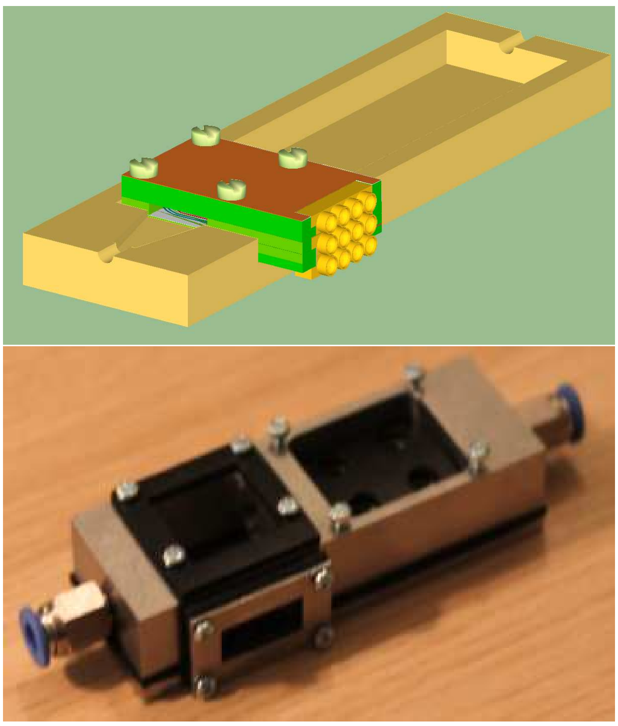

Fig. 3. Top: functionnal sketch of the full sensor cell bottom. The mylar membrane is in the bottom left part while, in the upper right part, four commercial sensors are installed. Bottom: corresponding realized cell

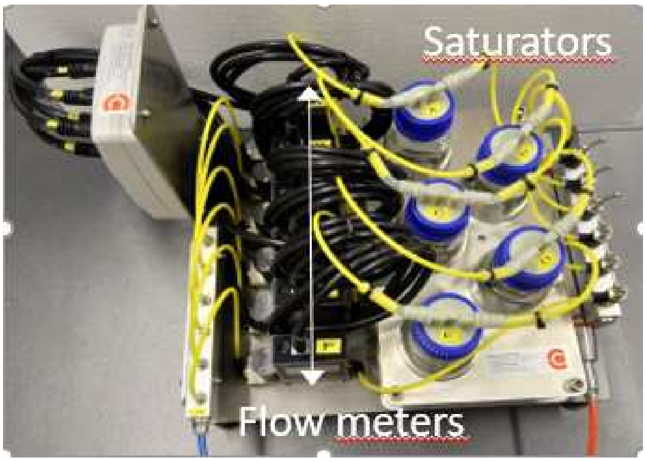

Fig. 4. Picture of the gas control system with 5 saturators and flow meters.

C. Sensor cell

The last transduction mean is more clearly presented Fig. 2 with all the functional elements using the bottom part amplifier. Mini coaxial connectors are used and three commercial sensors are added to monitor temperature, pressure and humidity. Those three parameters should be closely monitored as they influence strongly the different transduction mechanisms.

D. Full Sensor block

The sensor walls and access have been optimized to favor laminar transport of the gas in order to reduce diffusion time constants and inhomogeneous concentration repartition. The full sensor block is presented Fig. 3. It includes a second cell after the sensor's one that is used to add four auxiliary commercial gas sensors from Eurogas Management LTD. They monitor CO, NO_2, H_2S and Volatile Organic Compounds (VOC). This second cell will allow direct comparison of the measurements during the first stages and will naturally evolve to host another large membrane or integrated MEMS sensor in a future MIMO approach.

E. Gas control system and acquisition unit

The Gas control system is presented Fig. 4. It is designed for controlling/mixing five different gas accurately (10 sccm resolution) with state of the art response times (ms).

NI USB-6363 will provide a 16 differential ADC acquisition with 16 bits resolution at 2 MSamples/s for each This will allow post measurement processing in order to take advantage of the multiple outputs associated to a single input.

III. Analytical model of the membrane vibrations

In the analysis cell depicted Fig. 2, there are three main components that can be seen integrated fig. 3. The piezo ceramic actuator covers the active membrane with a mm size air gap. The actuator allows to control and excite the membrane mode of oscillation. On the other side of the membrane, an integrated voltage amplifier with one non-contacting electrode is approached very closely (air gap of 20-100 µm). The working principle of this set of components to get a micro balance use the resonant moving of the biased membrane, while the capture electrode of the amplifier monitors the membrane response by a capacitive effect. Two main transmission ways form the piezo-disc to the membrane can be efficient. The first one is from the acoustic pressure field in the cell gas, while the second one is though the constitutive solid materials that are used in the cell assembly. The first one acts directly upon the membrane, and it is a well-known academic problem [9]. The second one directly acts upon the material edge of the membrane. The modelling of that excitation is related to the precedent one, by solving the membrane movement equation with a forced moving boundary condition.

A qualitative analysis of our system led us to get an evaluation of the efficiency of these two ways to excite the membrane. The acoustic pressure in the gas should be dominant when the cell assembly is rigid and clamped to a large and heavy body. The second way is not often used because the overall assembly should be as light as possible and not rigidly clamped. This consideration probably explain why that problem conditioning was not found in the literature. Indeed, the first assembly of the cells was done using four stainless steel screws and a well clamped cell. Excitation of the membrane then did not produced sufficient response at the amplifier output. While mounting the cell using nylon screws without clamping then lead to large amplitude signals, making obtaining their spectra easy with an Ono Sokki analyzer. We then assumed that the excitation through the moving boundary condition was dominant in the later assembly type.

TABLE I. Model parameters

Symbols	Names	Values	units
L	square size	1-2	cm
h	membrane thickness	1-10	µm
ρ	density	1350	kg/m³
T_0	tension	1-50	N/m
c	wave speed	$\sqrt{T_0/\rho h}$	m/s
µ	viscosity	10^{-5} - 10^{-7}	s
$f_{n,m}$	Eigenmode	$\frac{c}{2L}\sqrt{n^2+m^2}$	Hz
$\beta_{n,m}$	damping factor	$\frac{\mu}{2}\left(\frac{\pi c}{L}\right)^2(n^2+m^2)^2$	/s

In the framework of the square geometry, the problem was analytically solved with time dependent boundary condition at the membrane edge. Given the parameters defined and gathered Table I., the magnitude of the displacement at the center of the membrane follows the expression for the fundamental mode (m=n=1):

$$q_{11}(t) = \frac{2\beta_{11}\Omega\cos(\Omega t) + (\Omega^2 - {\omega_{11}}^2)\sin(\Omega t)}{(\Omega^2 - {\omega_{11}}^2)^2 + 4{\beta_{11}}^2\Omega^2} * \frac{16\Omega^2 * q_0}{\pi}$$

Where q_0 is the amplitude of the edge variation and Ω its angular velocity.

That analytical model was used to evaluate the magnitude of the sensitivity parameters at the resonant frequency of the fundamental mode. Those parameters were defined with respect to the phase deviation around the resonant frequency (that would be used in the lock-in detection). We first evaluated the phase sensitivity to mass variation of the membrane. The result is shown Fig. 5 and 6, and a value of -30°/µg is obtained. We deduce the order of magnitude of the

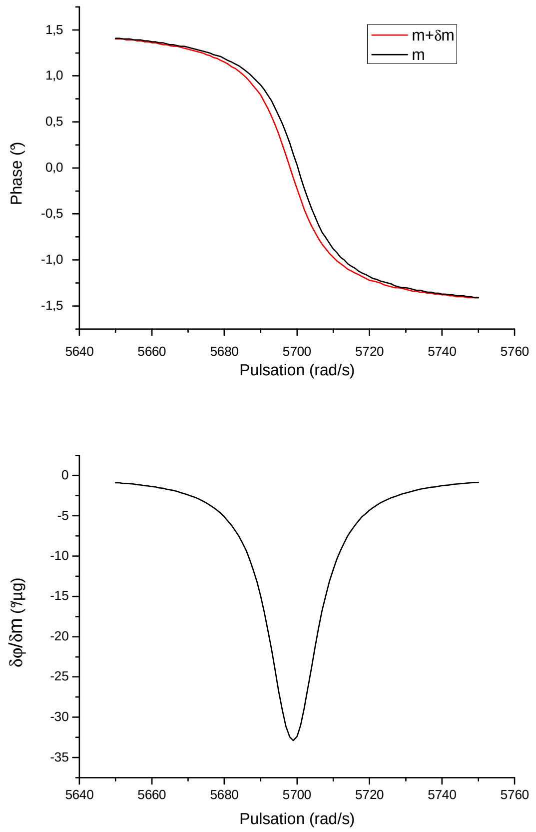

Fig. 5. Top : Curve presenting the phase shift relatively to the piezo excitation of the membrane when submitted to a 0.45 µg mass adsorption. Bottom: Extracted phase sensitivity to mass variation

mass resolution when a relative phase resolution of 360°/10^5 is assumed as a common value: $\delta m = 120\ pg$. For ethanol, this corresponds to 2.6 pmol. If we consider a cell gas volume of 1 cm^3 and the ideal gas law, the intrinsic ultimate resolution would be around 60 ppb of ethanol in air. This estimation is not taking into account the fact that only a fraction of the ethanol passing through the cell is effectively adsorbed.

Two other sensitivities have been evaluated using the model. Phase response to membrane thickness is -7°/nm with the expected same sign as the response to mass variation. And phase response to Tension is +20°/(mN.m^{-1}).

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