MODELING, DESIGN AND EXPERIMENTAL CHARACTERIZATION OF MICRO-ELECTRO-MECHANICAL SYSTEMS FOR GAS-CHROMATOGRAPHIC APPLICATIONS

ENRICO COZZANI
DEIS DOCTORATE CYCLE XXIII
**SCENARIO**

**GAS-CHROMATOGRAPHY:** analytical technique based on separative principle, applied to mixtures of pollutants at unknown concentrations.

**IN PARTICULAR:**

The principle of chromatographic separation is based on the specific affinity between the sample mixture and a “stationary phase” housed in a separation column.

---

**Carrier gas** (mobile phase)

- **Sample mixture**
- **Stationary phase**
- **Separation column**

**Signal**

- **$t_A$, $t_B$** = retention time
BLOCKS OF A GAS-CHROMATOGRAPHIC MODULE

✓ INJECTION SYSTEM
✓ SEPARATION COLUMN
✓ DETECTOR

CHROMATOGRAM
Since several years, the Institute for Microelectronics and Microsystems (IMM) - Section of Bologna is involved in an intense research activity focused on air quality monitoring.

In particular, a great concern is referred to the analysis of volatile organic compounds (eg. BENZENE) because of their strong toxicity even at extremely low concentrations (as a matter of fact, risk threshold is in the order of parts per billion (ppb)).

In this scenario, a thorough knowledge of MEMS (Micro-Electro-Mechanical-Systems) fabrication techniques provides a great contribution for the design of innovative microsystems employed in a gas-chromatographic module, characterized by reduced dimensions (and costs) and improved performances with respect to the actually disposable products.

TARGET: fabrication of the three blocks (injection system, separation column, detector) by exploiting silicon micro-machining techniques.
ELECTRO-THERMAL SIMULATIONS

The starting point of my doctorate activity was the development and the validation of a Finite Element Model (FEM) aimed at simulating the coupled electro-thermal behavior of the microdevices, in order to support and optimize their design.

The validation of the model was carried out by comparing the simulation results with the experimental characterization of a particular detector developed since 2005 at IMM – Section of Bologna, i.e. a Metal OXide (MOX) sensor, whose detection principle is based on the fact that when a thin film of metal oxide (specifically SnO$_2$), wired between two electrodes, interacts with a pollutant at unknown concentration, in proximity of 400°C mechanisms of oxidation-reduction take place and cause changes in the chemical and physical properties of the film (specifically, ELECTRICAL RESISTIVITY).

The analysis of the pollutant can be easily performed by monitoring the variations of the electrical current flowing through the electrodes.
MOX SENSOR DESIGN

By exploiting silicon micro-machining and photolithography definition techniques, chips containing arrays of four sensors are fabricated. Each sensor is formed by:

- A suspended thermally-insulated dielectric membrane
  \((\text{SiO}_2 - \text{Si}_3\text{N}_4 - \text{SiO}_2 \; \text{th} = 1 \mu\text{m})\)

- A “horseshoe-shaped” platinum heater \((\text{th} = 200\text{nm})\)

- Two concentric platinum electrodes contacting the sensitive film \((\text{th} = 200\text{nm})\)
The use of FEMLAB software enabled the coupling of the electrical behavior described by Poisson’s equation

\[ \nabla \cdot (\sigma \cdot \nabla V) = 0 \]  \hspace{1cm} (1)

with the thermal behavior described by Fourier’s equation

\[ Q = -\nabla (k \nabla T) + \frac{ht}{dA} \cdot (T - T_a) + \frac{ct}{dA} \cdot (T^4 - T_a^4) \]  \hspace{1cm} (2)

by means of Joule’s equation upon power dissipation in the form of heat

\[ Q = \rho(T) \cdot |I|^2 = \frac{1}{\sigma(T)} \cdot (\sigma(T) \cdot |E|^2) = \sigma(T) \cdot |E|^2 = \sigma(T) \cdot |\nabla V|^2 \]  \hspace{1cm} (3)

Putting eq. (3) in eq. (2), the relationship representing the fully coupled electro-thermal model can be easily disclosed:

\[ \nabla^2 T - \frac{ht}{k \cdot dA} \cdot (T - T_a) - \frac{ct}{k \cdot dA} \cdot (T^4 - T_a^4) + \frac{\sigma}{k} \cdot |\nabla V|^2 = 0 \]
Electrical, thermal and optical properties of all the thin film materials were experimentally measured by using appropriate test structures and the obtained values were employed in the model (no fitting parameters).

Simulations were carried out in two subsequent steps:

✓ Initially, sensor behavior “in vacuum” was considered (i.e. neglecting the contribution of air as heat conducting material) → 2D simulation

![Graph showing temperature vs. power with Err < 1%]
Following, the procedure was repeated considering the influence of air upon heat conduction → 3D simulation

The increase in relative error can be explained with the uncertainty in the evaluation of thermal conductivity of air (the formula of $k(T)$ used in the model was taken from literature) and with the fact that its dependence from relative humidity was neglected.
A limitation of valve-based devices is the small quantity of injected sample: pre-concentration devices have been designed to collect volatile compounds from large-volume vapor sample and inject them into the gas chromatographic column as narrow vapor plugs. Our unit is a micro-fabricated cartridge formed by channels filled with cavitands, able to trap the volatile compounds, and to subsequently purge them by a rapid thermal desorption controlled through an integrated platinum resistor.

**FABRICATION PROCESS**

1. **Silicon Wafer**
2. **DRIE etch**
3. **Pt deposition**
4. **Bonding pyrex**
5. **Oxide deposition**

**Materials:**
- **PYREX (300µm)**
- **OXIDE (100nm)**
- **SILICON (500µm, 300µm etched)**
- **PLATINUM (240nm)**
CHIP WIDTH = 1.4cm
CHIP LENGTH = 2.5cm

CHANNEL WIDTH = 1mm
CHANNEL SEP = 0.2mm

Rheater @ Tamb = 12Ω
RTsensor @ Tamb = 100Ω

ELECTRO-THERMAL 3D SIMULATION

\[ \approx 600 \text{ mW} \]
\[ @ 200^\circ \text{C} \]
SEPARATION COLUMN

The doctorate activity proceeded focusing the attention on the design and fabrication of micro-machined silicon packed columns that specifically execute chromatographic separation.

1st PROTOTYPE: 50 cm long double-spiral shaped column (1 inlet & 1 outlet), rectangular section, fabricated on a 2.5 x 2.5 cm² chip:

\[ \text{Step} = \text{W} + \text{Sep} \]
\[ \text{W} = \text{channel width} = 800 \, \mu\text{m} \]
\[ \text{Sep} = 100 \, \mu\text{m} \]
ELECTRO-THERMAL 3D SIMULATION

12Ω @RT
≈ 850 mW
@ 200°C
2nd PROTOTYPE: 1m long double-spiral shaped column (1 inlet & 1 outlet), rectangular section, fabricated on a 2.5 x 4.5 cm² chip:

12Ω @ RT
≈ 1.27 W
@ 200°C
PICTURES

METAL (chip front)

HOLMES (chip rear)

STATIONARY PHASE: Carbograph 2 + 0.2% Carbowax
EXPERIMENTAL RESULTS

Chromatogram of a VOC’s mixture (BENZENE, TOLUENE, ETHYL-BENZENE, M-XYLENE @ equal concentrations).

Time of analysis: 10 minutes
FAST GC: CAPILLARY COLUMNS

Miniaturized, portable fast-GC systems based on very low inner diameter (≤ 100 µm) capillary columns are emerging, allowing for vastly improved separations with higher resolution. Other merits include complete chromatogram acquisitions in few minutes, smaller sample size requirements and often higher sensitivities.

Chip = 2 x 2 cm²
Column length = 2m
Circular section
Diameter = 100µm

Step = W + Sep
(W = 20 µm, Sep = 120 µm)

ISOTROPIC ETCH
EXPERIMENTAL RESULTS

VOC’s MIXTURE INJECTED IN A 2m-LONG CAPILLARY COLUMN:
1 – Benzene; 2 – Toluene; 3 – ethyl-benzene; 4 & 5 – Xilene-isomers

Time of analysis: 2 minutes
FAST GC: DETECTOR

Analysis cycle should be around \([1 \div 5]\) minutes and typical column flow rates for fast-GC stand inside the \([0.1 \div 0.5]\) sccm range. For these reasons, fast-GC requires detectors with extremely low volumes (absence or reduction of dead volumes).

The adopted solution consisted in the fabrication of a integrated pyrex micro-chamber in order to encapsulate the detector in a ultra-low volume (\(\approx 0.1\mu L\)). Preliminary simulations were performed on MOX sensors, implementing the electro-thermal model with a microfluidic part governed by the Navier-Stokes equations:

\[\begin{align*}
\frac{\partial u_i}{\partial x_i} &= 0 \\
\rho \cdot u_j \frac{\partial u_i}{\partial x_j} + \frac{\partial p}{\partial x_i} &= \mu \cdot \frac{\partial^2 u_i}{\partial x_i \partial x_j}
\end{align*}\]
THERMAL CONDUCTIVITY DETECTOR (TCD)

Although chemical MOX sensors showed an excellent sensitivity towards VOC’s, they can not be considered as “general purpose” detectors. TCD, whose operation principle is purely physical, is still today the most used detector in portable GC systems because of its “universality”.

\[
\text{If } R_1 \cdot R_4 = R_2 \cdot R_3 \rightarrow V = 0 \\
\text{(NO pollutant)}
\]

\[
\text{If } R_1 \cdot R_4 \neq R_2 \cdot R_3 \rightarrow V \neq 0 \\
\text{(YES pollutant)}
\]

Reference gas (carrier) flow comes from an empty capillary column, while analytical (carrier + pollutant) flow comes from a capillary column filled with stationary phase.

2 columns needed
FABRICATION PROCESS

Si Wafer (500µm) → membrane deposition → RIE etch

Pt deposition → TMAH etch → pyrex bonding

Reference channel: 170 µm
Analytical channel: 650 µm

18/01/2011
Enrico Cozzani
Chip: 5 x 5 mm²

Diss Pow = 40mW for AIR carrier
Diss Pow = 200mW for HELIUM carrier
PRELIMINARY RESULT ON TCD

TCD connected to a commercial GC-system: not its own control electronics for biasing and reading + extra dead volumes introduced

injection

2% toluene in He

43mV
FUTURE ACTIVITIES

✓ Improve performances of the capillary columns (increase length or decrease inner diameter).

✓ Characterize TCDs with their own electronics.

✓ Exploiting the same fabrication process, design a mixed array of sensors, to combine the high sensitivity of MOX and the universality of TCD.

✓ Design and fabricate the first prototype of a silicon micromachined injector (ongoing…..).

✓ Assembly the whole in order to fabricate a portable micro-GC with high performances and reduced dimensions (and costs).

😊 THANKS FOR YOUR ATTENTION 😊