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First approach to the use of liquid crystal elastomers for chemical sensors

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Abstract

Liquid crystalline thin films elastomers that are able to bind pesticides have been developed. The synthesis involves grafting mesogen and crosslinkable groups on a polysiloxane chain in the presence of a template molecule. The molecular imprinted material is obtained after thin film deposition, UV crosslinking and washing. Experiments of readsorption of pesticide are presented. Development of a multisensor platform based on thermal and capacitive sensors is described and tests of deposition of the polymer film are presented.

Keywords: Liquid crystal; Molecular imprinted polymers; Pesticide; Recognition component; Sensors

1. Introduction

The molecular imprinting technique is a valuable method for preparing materials able to mimic the molecular recognition phenomena present in living systems. These are synthesized by polymerizing and crosslinking monomers in interaction with a chosen template. After removal of this by washing steps, the material presents specific cavities that are complementary in shape and size to the template (Scheme 1). Most drawbacks of this method have been linked to the need for a large amount of crosslinking agent (usually around 80–90%) to restrict distortion phenomena of the polymer backbone. In order to overcome this problem, we have recently developed new molecular imprinted polymers (MIPs) using liquid crystal elastomers [1]. Owing to the physical crosslinking of the mesogens, low chemical crosslinking (below 15%) has been found sufficient to induce recognition properties by the MIP. In this first approach, the synthesized materials were quite thick membranes (0.6 mm) without any control of the thickness. In our continuing studies on this subject, we wish to report in this article a first approach to use these liquid crystalline MIPs in chemical sensors. This implied the elaboration of thin films having a controlled thickness and the design of suitable sensor platform. In this study, the chosen template is diazinon, an organophosphorus pesticide. Although numerous methods for the detection of such species have been proposed, only few are both sensitive and simple to carry out. The need for sensors that would be small, very sensitive and selective to the desired pesticide is still high. The molecular imprinting method has already been applied in the field of sensors using different types of detection [2]: weighing with a quartz crystal microbalance (QCM), capacitance or conductance measurements, fluorescence or other spectroscopic methods. There are several examples of solid phase extraction of insecticides based on MIPs in which the material is aimed at preconcentrating the insecticide to be characterized by chromatography [2–5]. Concerning MIP-based sensors, several studies have reported the detection of organophosphate pesticides [6–10]. The limit of detection was in some cases as low as 7 ppt. However, very often, these materials lack selectivity between closely related molecules. This communication represents the first step towards new MIP-based sensors that are controllable by an external stimulus. Furthermore, developments in the field of silicon micro

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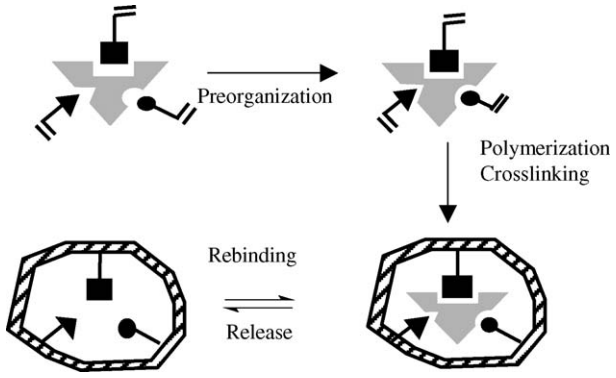


Scheme 1. Molecular imprinting technique.

fabrication techniques offer advanced technologies to improve the domain of sensors applications.

2. Experimental

2.1. Materials

Solvents were dried over CaH_2, distilled, and degassed before use when necessary. 4-Methoxy-4'-(3-butenyloxy)phenyl benzoate was synthesized as previously described [11]. Polyhydrogenomethylsiloxane ($\overline{DP_n} = 80$) (ABCR), diazinon (AB7 Industries) and dichlorodicyclopentadienyl-platinum II (Strem) were used as received.

2.2. Characterizations

^{1}H NMR spectra were recorded on a Bruker AC 250 spectrometer at 250.13 MHz. ^{13}C and ^{29}Si NMR spectra were recorded on a multinucleus Bruker DPX400 spectrometer, respectively, at 100.61 and 99.36 MHz. IR spectra were carried out on a Perkin-Elmer FTIR 1760X spectrometer. HPLC was performed on a column from Waters XTerra RP 18 (eluent acetonitrile/water 80/20, flowrate 1 mL min^{-1}).

2.2.1. 4-(10-Undecenyloxy)benzophenone

Ten grams of 4-hydroxybenzophenone (50.4 mmol), 8.6 g of 10-undecenylalcohol (50.5 mmol) and 13.2 g of triphenylphosphine (50.4 mmol) were dissolved in 100 mL of THF. A solution of 8.8 g of diethylazodicarboxylate (50.5 mmol) in 50 mL of THF was slowly added at 10 °C. The resulting solution was stirred during one night at ambient temperature. The solution was concentrated and 50 mL of cyclohexane/ethylacetate 20/5 (v/v) was added to precipitate triphenylphosphineoxide and diethyloxycarbonyl hydrazine. The product was recrystallized twice from cyclohexane. Yield: 9.0 g (51%). ^{1}H NMR: 1.2–1.6 (m, 12H, CH_2); 1.8 (m, 2H, CH_2–CH_2–O); 2.04 (m, CH_2–CH=CH_2); 4.0 (t ^{3}J = 6.6 Hz, CH_2=O); 4.95 (m, 2H, CH_2=); 5.8 (m, 1H, CH=); 6.95 (d ^{3}J = 8.8 Hz, 2H, *o*-aromatics); 7.4–7.9 (m, 7H, aromatics). ^{13}C NMR: 195.6 (C=O); 162.9 (C_{Ar}–O); 139.2 (CH=); 138.4, 132.6, 131.8, 130.0, 129.9, 128.2 (aromatics); 114.2 (=CH_2 and C_{Ar}); 68.3 (CH_2–O); 33.8 (CH_2=); 28.9–29.5 (CH_2); 26.0 (CH_2–CH_2–CH_2–O). IR (KBr pellet) $\bar{\nu}$ (cm^{-1}): 3080 w (aromatic and vinylic CH stretching), 2921, 2850 str (aliphatic CH stretching), 1640 str (CO stretching), 1603 str (C=C), 1291, 1308 m, 1255 str (Ar–O), 1175, 1149, 1018, 911, 847, 795, 739 m, 692 str (aromatics). EI mass spectrum (relative intensity): 350 (51) M^+, 198 (46) M^+ − undecadiene, 121 (80), 105 (38), 77 (29) phenyl, 55 (79), 41 (100) propenyl. High resolution MS ESI: th. 351.2324 ($M + H^+$); exp. 351.2425.

2.3. Hydrosilylation reaction

Polymethylhydrogenosiloxane (1.3 mmol of SiH groups), 1.36 mmol 4-methoxy-4′-(3-butenyloxy)phenyl benzoate (105 mol% relative to the polymer units), 0.067 mmol 4-undecenyloxybenzophenone (5 mol%) and 0.13 mmol of diazinon (10 mol%) were mixed with 3 mL of degassed toluene under argon atmosphere. To this solution was added about 2.5 μmol of $C_{10}H_{12}Cl_2Pt$ in 0.5 mL of degassed toluene. The resulting mixture was stirred for 65 h at 70 °C under argon atmosphere. Toluene was evaporated and the resulting polymer was kept in the dark until use in films. ^{1}H NMR: 0.23 (br s, Me–Si); 0.6–0.8 (m, –Si–CH_2–); 1.0–2.0 (m, CH_2); 3.8–4.0 (3 br s, CH_2–O and Me–O); 6.8–7.4 (m, aromatics); 7.5–7.9 (m, benzophenone aromatics); 8.0–8.3 (mesogen aromatics). ^{13}C NMR: 165.5, 164.2 (C_{Ar}–O); 157.1 (C_{Ar}–O); 144.7 (C_{Ar}–OCO); 138.4, 132.5, 130.8, 129.4, 128.6, 126.4, 125.7, 122.9, 115.5, 115.3, 114.1(aromatics); 69.4, 68.2 (CH_2–O); 55.7 (MeO–); 33.2, 20.0, 17.8 (CH_2); 0.3 (Me–Si). ^{29}Si NMR: −22.5 (O–Si–O).

2.4. Films of polymer

The polymers were spread on substrate with 25 or 70 μm thickness spacers in the isotropic state (75 °C). Films of about 2 cm^2 surface area were obtained. The layers were then irradiated at 50 °C during 40 min with a Xenon lamp equipped with a high pass filter at 335 nm, in order to crosslink the polymer through the reaction of benzophenone.

2.5. Microfabrication process

Sensors were performed on 100 mm silicon wafers. The process consisted in 12 leading stages with six photolithographic masks:

1- Low pressure chemical vapor deposition (LPCVD) of silicon oxide (SiO_2) and of silicon nitride (SiN_x) films. The total thickness of the layer was 1.4 μm.
2- Deposition (LPCVD) of a doped polysilicon layer (e: 0.5 μm).
3- Photolithography (Mask 1) and chemical etching to pattern the polysilicon layer.
4- Passivation with a plasma enhanced chemical vapor deposition (PECVD) SiO_2 layer (*e*: 0.1 μm).
5- Photolithography (Mask 2) and chemical etching of the SiO_2 layer in order to open electrical contacts with the polysilicon layer.

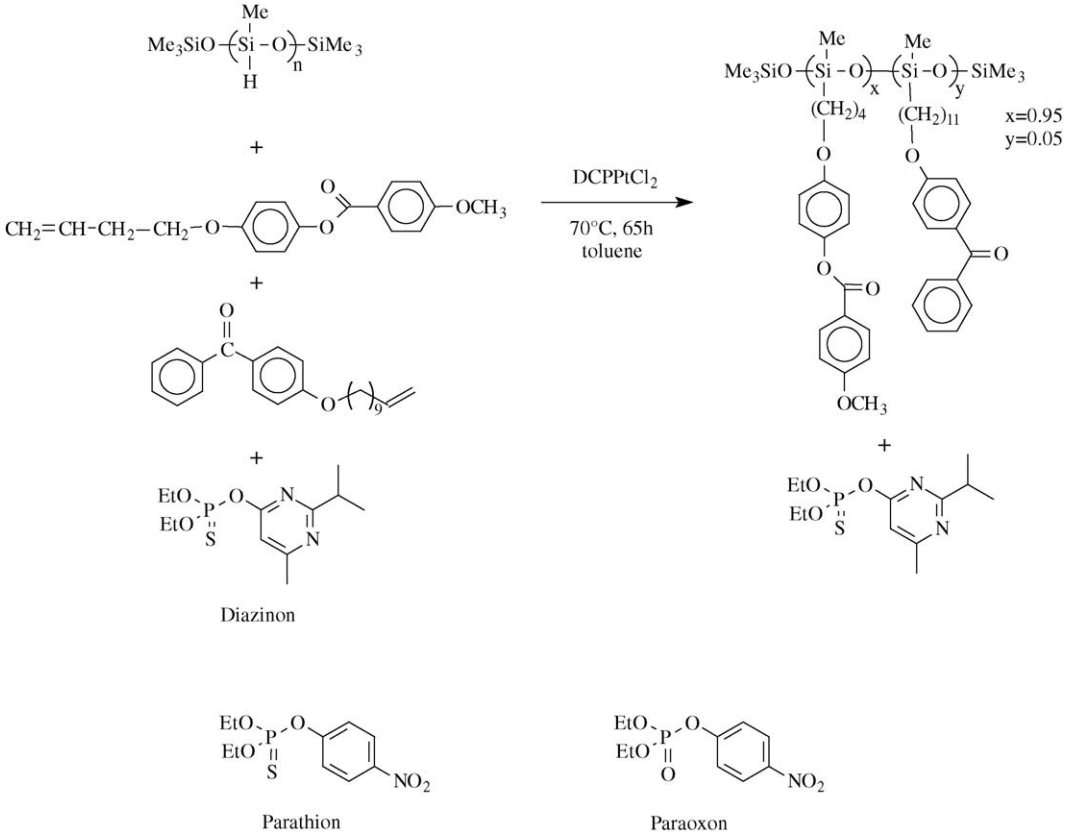
6- Deposition of titanium (*e*: 0.1 μm) and gold (*e*: 0.8 μm).
7- Photolithography (Mask 3) and chemical etching to pattern the Ti/Au electrodes.
8- Passivation with PECVD SiO_2 layer (*e*: 0.1 μm).
9- Photolithography (Mask 4) and chemical etching to open the SiO_2 layer over the gold electrodes and the connecting pads.
10- Photolithography (Mask 5) to pattern the bottom layers of the wafer.
11- Photolithography (Mask 6) to pattern the tank for liquid crystal elastomers.
12- Anisotropic chemical etching of the silicon with KOH to release the membrane.

3. Results and discussion

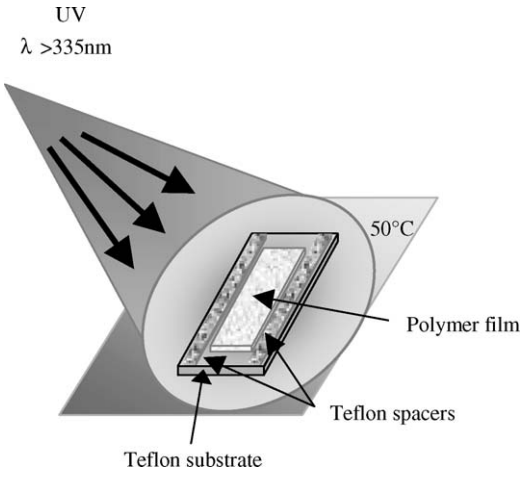
3.1. Synthesis of liquid crystal elastomer

The imprinted polymer networks used here were synthesized in two steps, starting from commercial polyhydrogenomethylsiloxane chains ($\overline{DP_n} = 80$). The first step consisted in the synthesis of the side chain liquid crystalline polymer in the presence of diazinon as template molecule according to Scheme 2. The linear polymer was synthesized via a hydrosilylation reaction between hydrogenomethylsiloxane units and two appropriate terminal alkene side chains using dichlorodicyclopentadienyl-platinum as catalyst. The first chosen substituent was 4-methoxy-4'-(3-butenyloxy)phenyl benzoate that exhibits a monotropic nematic mesophase (melting point 96.9 °C, isotropic to nematic transition temperature 50.6 °C) [1]. The second side group was 4-undecenyloxybenzophenone that presents a photoreactive group [11]. The synthesis was carried out in the presence of diazinon in order to imprint its shape in the material. In a first step, complex formation between diazinon and an aromatic acid was tested, but none could be observed either by ^{1}H NMR or IR spectroscopy, owing to a very low pK_A of diazinon. Therefore, a simple system containing diazinon and a liquid crystal molecule was synthesized, and we assumed at that time that π–π stacking could take place between the pesticide and the liquid crystal aromatic cycles leading to enough interaction for a recognition process to take place in the material, as already reported for other MIPs [8]. Two sets of polymers were synthesized: the first one in the presence of 10 mol% of pesticide (versus Si–H groups), and the second one without it as a blank material.

Almost 3 days at 70 °C were necessary to obtain complete conversion of silane functions by hydrosilylation as checked by the disappearance of Si–H signal at 4.8 ppm in the ^{1}H NMR spectrum of the polymer. In order to avoid untimely crosslinking due to residual Si–H functions, an excess of olefin molecules was used. In some cases, a low percentage (∼10%) of isomerization of the double bonds was observed during the synthesis as revealed by an additional signal at 5.8 ppm. Optical microscopy and differential scanning calorimetry studies showed that the polymer without diazinon exhibited a glass transition temperature at −13 °C and a nematic to isotropic transition at 63 °C.



Scheme 2. Grafting of mesogens and benzophenone moieties and other pesticides used in this study.



Scheme 3. Polymer film design.

The fully substituted polysiloxanes with this crystal liquid group has been shown to exhibit a liquid crystalline behaviour until 104 °C [12]. The difference observed between this case and our polymer may be attributed to the fact that the polymer contained 5 mol% of benzophenone derivative, and liquid crystal molecules in excess.

In a second step, the polymers were spread on Teflon substrate with thickness spacers (25 or 70 μm) in the isotropic state (75 °C) according to Scheme 3. The layers were then irradiated at 50 °C above 335 nm during 40 min. The benzophenone moiety used on the polymer shows absorption bands at 298 and 340 nm. This absorption is different from the absorption band of the liquid crystal moieties (293 nm) and is caused by a n,π^* transition in the carbonyl group, the resulting triplet being a diradical. The oxygen radical can then abstract a hydrogen atom from the C–H bonds of methyl groups of the polymer, leading to crosslinking of the material. After UV-curing, the materials looked like yellowish elastic films and weighed between 3 and 11 mg. This colour might result from secondary reactions due to the presence of aromatic groups or remaining traces of hydrosilylation catalyst. The films were then washed with acetonitrile in order to remove the pesticide molecule as well as unfixed liquid crystal. This solvent was chosen for its ability to dissolve both molecules and the fact that it is a poor solvent for the polymer. Therefore, small molecules could be extracted from it without any large swelling. The washing process was followed by HPLC and no significant variation occurred after three washings of 4 h each. The amount of template released from imprinted materials was about 80% of the theoretically incorporated diazinon. The thickness of the films was measured by profilometry and was found close to 40 μm for spacers of 70 μm. This difference was attributed to the evaporation of solvent still present during spreading of the films.

3.2. Adsorption capacities of the films

Batch rebinding studies were then carried out by letting the washed films in contact with fresh solutions of diazinon in water/acetonitrile 80/20 during 72 h, which was well after

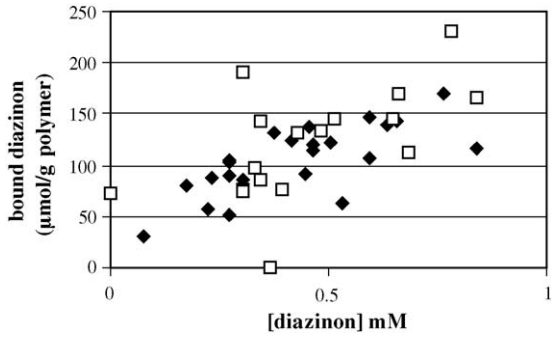
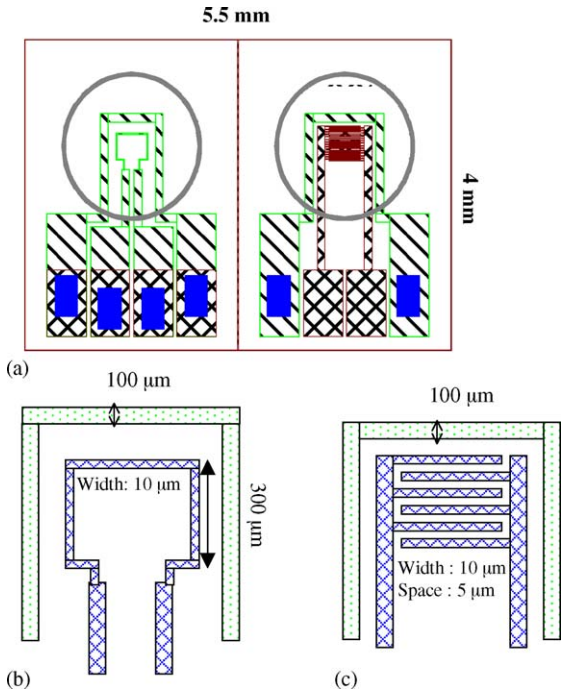


Fig. 1. Readsorption of diazinon on polymer films as a function of diazinon concentration. Squares: non-imprinted polymer; filled diamonds: imprinted polymer.

the equilibrium has been reached (typical time for equilibrium 16 h). Due to a very poor solubility of diazinon in pure water (limit of solubility: 5×10^{-8} M), studies in this solvent were observed to have an erratic behaviour. The results with variable concentrations of diazinon in water/acetonitrile 80/20 are presented in Fig. 1. Readsorption of diazinon was quantified by HPLC. Both imprinted or non-imprinted films were able to readsorb at least up to 150 μmol of diazinon per gram of polymer without showing any sign of saturation, which is approximately 50% of the initial loading. Compared to other already published results [1], the capacity of these films was further increased, but the concentration range being different this result will have to be verified. Preliminary batch rebinding tests showed that from a saturated parathion solution, between 30 and 60% could be trapped by the material (not imprinted or imprinted with diazinon), whereas paraoxon was not retained at all. This was attributed to differences of polarity between phosphonate and thiophosphonate species. However, unfortunately, no imprinting effect could be observed from Fig. 1, contrary to what was shown on our previous systems where covalent bonds or H-bonded complex formation between the template molecule and the monomers were present. Furthermore, since the films used here are a lot thinner than in our first experiments, surface non-specific interactions might be more important compared to thick bulk materials. The absorption phenomenon observed here and its selectivity could be attributable to the presence of the aromatic liquid crystal groups, as observed in chromatography towards aromatic molecules using liquid crystalline stationary phases [13,14]. However, our results show that π–π interactions might not be by themselves sufficient to lead to efficient imprinting phenomenon, even in liquid crystal elastomers. The synthesis of other systems leading to stronger interactions is therefore under progress.

3.3. Development of a multisensor platform

The second part of this work consisted in developing a multisensor platform that is compatible with the method used for the synthesis of the polymer film. It comprises a thermal sensor and a capacitive sensor. The process is based on micro electronics technologies, i.e. conventional chemical vapor deposition (SiO_2,



Scheme 4. Schematic representation of the sensing platform: (a) general overview showing the thermal sensor (left) and the capacitance sensor (right); (b) structure of the thermal sensor; (c) structure of the capacitive sensor.

SiN_x, polysilicon, . . .), sputtering deposition (Au, . . .) and photolithography. The overall structure of the sensing platform is given in Scheme 4 and photographs are shown in Fig. 2. The thermal sensor consisted in a 300 μm × 300 μm square resistance made with doped polysilicon, the line width was 10 μm and the thickness of the polysilicon layer 0.5 μm. The thermal sensor was surrounded by an outlying resistance, which is the heating element. The capacitive sensor consisted in an array of interdigited microelectrodes composed of 28 gold strips: their width was 10 μm and the interspace between electrodes was 5 μm. A surrounding polysilicon resistance (like on the thermal sensors) allowed the thermal regulation of the sensor. When necessary, an annular reservoir made of an epoxy photoresist (SU-8) was synthesized on top of the interdigited electrodes and heated area in order to delimitate the sensing area. To improve the sensitivity, sensors were performed on a dielectric suspended membrane.

After completion of the silicon sensor, the last step was the deposition of the liquid crystalline polymer over the sensing area. This step was crucial as it takes place at the end of the technological process and as its influence on the sensor performances is high. It should be compatible on one hand with the mechanical fragility of the suspended membrane, and on the other hand with physicochemical characteristics of the polymer. The liquid crystal elastomer could be coated on sensors collectively or individually. Two ways of deposition have been investigated: spin coating and micro syringes deposition. The former one is a conventional technique and enables the precise control of the layer thickness with an excellent reproducibility. However, it leads to a large polymer consumption. On the contrary, the latter one saves material but necessitates a high positioning accuracy and a high control of deposited volumes.

For spin coating, several parameters have an influence on the thickness and the homogeneity of the layer of liquid crystal elastomers: the speed and acceleration of the spin coater, the use of cover during spin-coating or not. Various tests were performed to optimise these parameters. The best homogeneity and reproducibility were obtained for a speed of 5000 r/min, an acceleration of 5000 r/min^2 and duration of 30 s when the cover was closed or a speed of 1000 r/min, acceleration of 1000 r/min^2 and duration of 90 s when the cover was open. These conditions allowed the formation of homogeneous 400 Å thick layers. The main advantage of this coating technique is that it is collective, i.e. the coating is carried out in one step on all sensors. Microsyringes deposition were also investigated. A small droplet was deposited in the SU-8 reservoir by the mean of the microsyringe. However, the deposited volume could not be easily and precisely determined.

4. Conclusion

This study constitutes the first approach to use liquid crystalline elastomers in chemical sensors. The synthesis of the precursor polymer, its processing into thin films and the crosslinking on the sensors have been described and optimised. However, the interactions between diazinon and the polymer are too weak to induce any imprinting effect. Therefore, a new pesticide that will lead to stronger interactions with the polymer is under consideration and the synthesis of imprinted liquid crystal elastomers with the new molecule will be carried out.

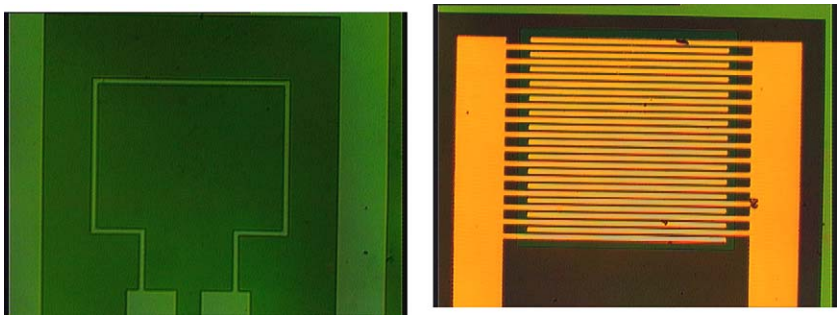


Fig. 2. Photographs of the thermal and capacitive sensor showing the heating resistance and the interdigited electrodes.

For the sensor part, capacitive measurements will be performed in order to assess the concentration range available for the detection.

Acknowledgments

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