*sensors*

*Invited Paper*

# Multiparametric Porous Silicon Sensors

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**Abstract**: We investigated the possibility of using several sensing parameters from porous silicon in order to improve gas selectivity. By fabricating porous silicon optical microcavities, three independent quantities can be measured, *i.e.* the electrical conductance, the photoluminescence intensity, and the wavelength of the optical resonance. We monitored the change of these three parameters as a function of $NO_2$ (0.5-5 ppm), ethanol (300-15000 ppm) and relative humidity (0-100%). Preliminary results confirm that the examined species affect the parameters in a different way, both as a relative change and as dynamic.

## Introduction

Porous silicon is well-known, inexpensive, integrable with silicon technology, and very sensitive to the environment due to its large surface versus volume ratio [1]. However, to date, discrimination of different substances in unknown mixtures by porous silicon is not yet possible, unless it is introduced to an electronic nose array [2].

We enhanced the sensing capability of porous silicon by using an optical microcavity made of porous silicon (Porous Silicon Microcavity, PSM), which operates as a multiparametric pollutant sensor. The device was tested in a controlled environment of variable composition. Several parameters were monitored simultaneously. The sensing parameters were the electrical dc conduction, the photoluminescence intensity, and the position of the peak of optical cavity. These parameters provide

three independent pieces of information, since they depend differently on the involved physical effects. Such amount of information cannot be extracted by using single layer porous silicon sensors.

## Experimental

The PSM were produced by electrochemical etching of $p^+$ type (0.005-0.02 $\Omega$ cm) silicon wafers. The cavity structure was a Fabry-Perot resonator with Distributed Bragg Reflectors (DBR), made of stacks of high index layers alternated with low index layers. We fabricated 8 period DBR and a spacer with intermediate porosity. Usually PSM are realized with highly p-type doped ($p^+$) substrates because the resulting PS layers are much easier to process and mechanically less fragile than those obtained with lightly p-type doped (p) silicon substrates. Unfortunately, the PL quantum efficiency of PS formed on $p^+$ doped substrates is very low ($\approx 10^{-2}$%) [4], but it is still detectable with our experimental apparatus. For electrical measurements we prepared a single porous layer (thickness 10 $\mu$m, porosity 65%) starting from the same wafer used for PSM realization. Two gold contacts were sputtered on the top surface of PS for electrical measurements.

The electrical and optical measurements were performed simultaneously in a chamber with a large quartz window and four tips for electrical measurements. Inside the chamber the operational conditions of the gas sensor were reproduced in a controlled and repeatable way. The method was based on volumetric gas mixing through mass flow controllers using certified bottles of gases diluted in dry air. The chamber was mounted on an optical bench equipped with an air-cooled Ar laser, a single monochromator, and a CCD detector for conventional photoluminescence measurements.

We performed electrical tests by a volt-amperometric technique at a constant bias of 1V. Dry air, $NO_2$, and ethanol of up to 1000 ppm were channelled from the certified bottles, while for higher concentrations of ethanol and for relative humidity the flow-through saturation method was used [5]. The carrier (dry air) passed through a condenser, which was kept at T=20 °C and placed after a bubbler (T=40 °C). At the outlet of the condenser the flow was saturated with vapours. The saturated vapour was diluted with synthetic air in the desired percentage. Temperature was kept at 20 °C during the characterization.

## Results and Discussion

As previously shown [6], $NO_2$ causes an increase in DC current. Current that flowed through the porous layer was reversibly increased when $NO_2$ was introduced into the test chamber at a concentration as low as 0.5 ppm. The reaction is completely reversible after dry air was restored (see Figure 1). The relative response towards 0.5 ppm was 2, and the response and recovery times were about one minute.

In the same time we observed modifications to the optical properties of the microcavity (see Figure 2). A decrease in the peak intensity was observed after 5 ppm of $NO_2$ was introduced into the chamber. The PL quenching began soon after the gas introduction and was halved after 30 minutes. The full recovery of the PL intensity was much slower (Figure 2 reports the spectrum taken after 1

hour) but after about one day the intensity recovered to the initial value. As expected, no peak shift was observed for $NO_2$ since the peak shift is related to the variation of effective refractive index.
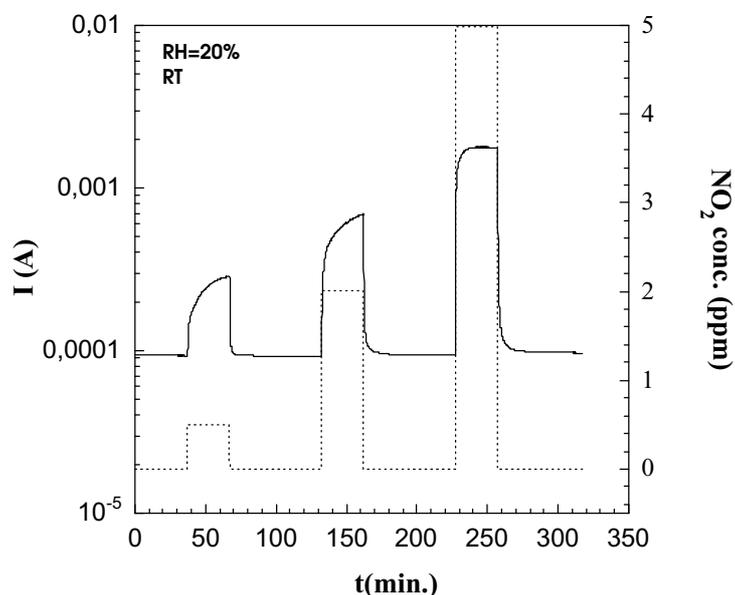


**Figure 1.** Dynamical electrical response of the device to 0.5, 2 and 5 ppm of $NO_2$. Measurements were carried out at RT and at 20% RH.
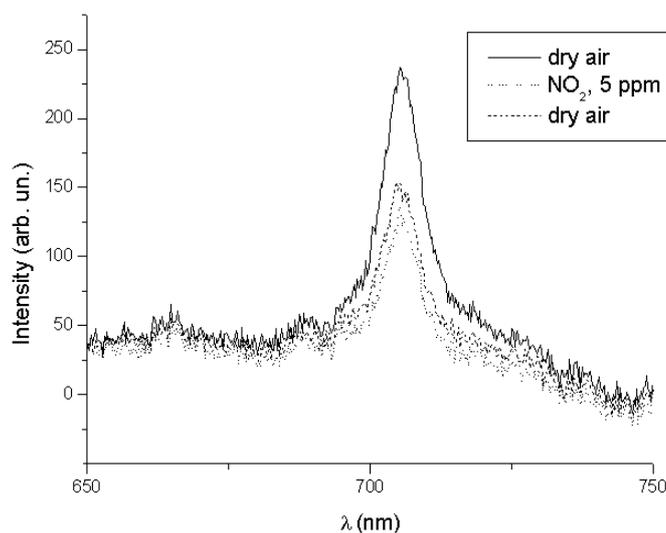


**Figure 2.** PL spectra of a $p^+$ PSM, under a controlled flow of dry air (solid line), dry air + $NO_2$ (5 ppm, dash-dotted line), and back to dry air (dashed line).

The behaviour of the mutiparametric sensor with ethanol was also tested. Current decreases reversibly as ethanol was introduced into the test chamber. The lowest concentration detectable with

DC current measurements was 300 ppm diluted in dry air. Figure 3 reports the current variation as 7500 ppm of ethanol was introduced into the test chamber.
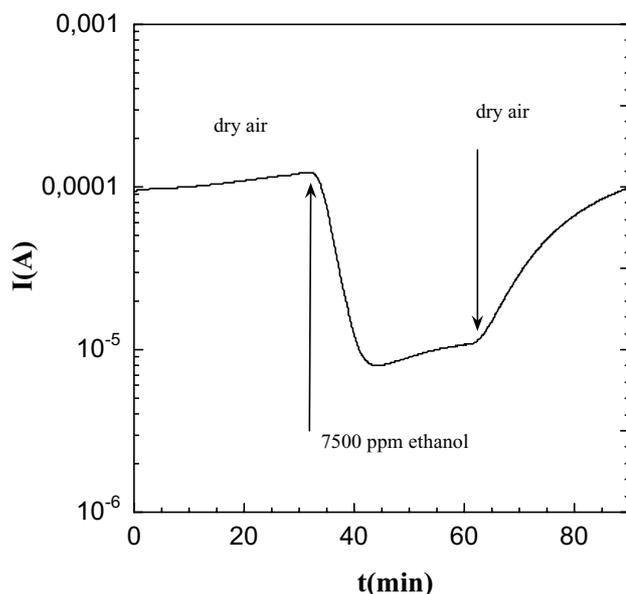


**Figure 3.** Dynamic electrical response of the device towards 7500 ppm of ethanol in dry air.

The effect of ethanol on PL peak shift and intensity is reported in Figure 4. A peak shift of about 2 nm can be observed after about 1 minute due to partial ethanol condensation into the pores. The peak shift is lower than that observed with p-type PSM [7]: this effect can be ascribed to lower percentage of vapour condensation due to higher dimension of the $p^+$ type pores than p type pores.
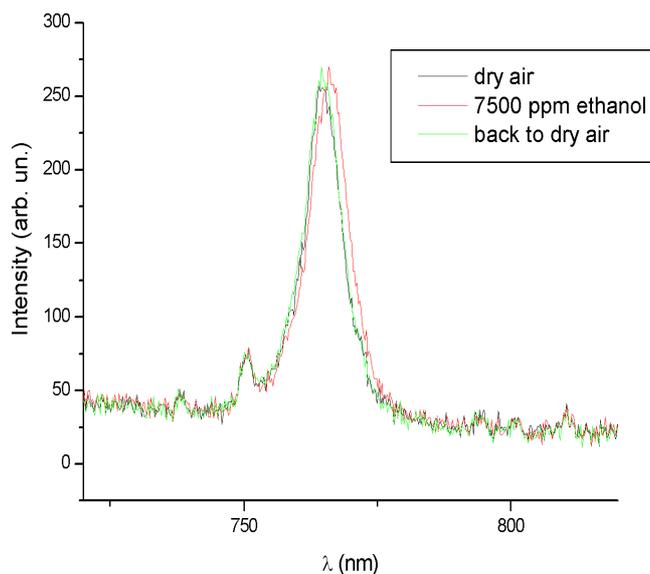


**Figure 4.** PL spectra of $p^+$ PSM, under controlled flux of air containing ethanol, at RT. Spectra have been acquired 10 minutes after the switching of the flux with the indicated concentration.

The variation of the PL intensity was small and not monotonous. In fact, ethanol caused PL quenching, but the simultaneous peak shift can place the cavity peak in a region of the spectrum with higher PL efficiency, thus justifying the PL increase.

An effect similar to that observed with ethanol was observed with humidity. Since refractive index of water (n=1.33 at 20°C) is lower than that of ethanol (n=1.36 at 20°C) the change in the effective refractive index of the porous matrix is lower with humidity, thus leading to a lower peak shift. Due to low PL efficiency the signal of $p^+$ type PSM is noisy so such a small peak shift is not easy to be observed in PL measurements. The peak shift can also be obtained at low signal to noise ratio from the reflectance measurements, thus allowing the detection of humidity variation lower than 40%. Peak shift observed from reflectance measurements was of 0.4 nm with 50% humidity.

The conductance measurement is much more sensitive to water, as can be observed in Figure 5. A reversible decrease was detected: conductance decrease of one order of magnitude variation is associated to humidity content changes from dry to 60 %.
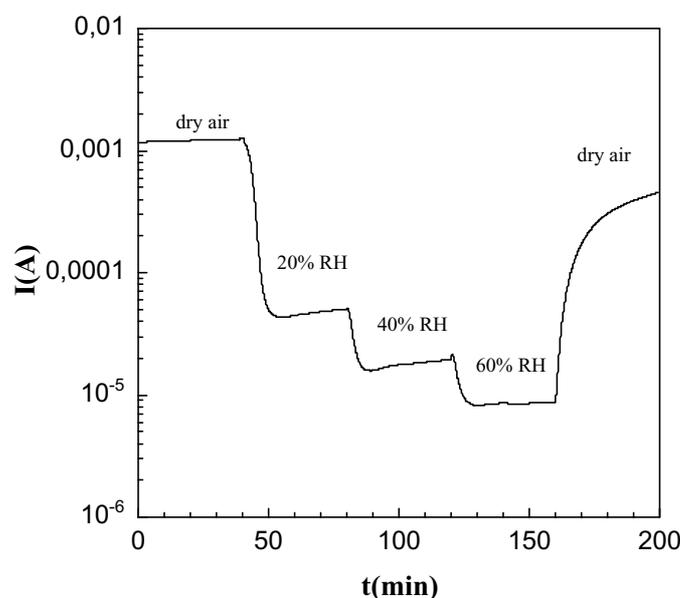


**Figure 5.** Dynamic electrical response of the device towards stepwise changes in relative humidity at RT.

These preliminary measurements, summarized in Table 1, show that it is possible to distinguish between a pollutant like $NO_2$ and interfering gases like humidity and ethanol by coupling the measurement of optical and electrical quantities in porous silicon.

**Table 1.** Effect of gases on 3 parameters of Porous Silicon Microcavity.

|  | DC current | PL Intensity | Peak shift |
|---|---|---|---|
| **$NO_2$** | Increase | Decrease | None |
| **Humidity** | Decrease | Vary | Red shift |
| **Ethanol** | Decrease | Vary | Red shift |

The decrease in DC current can be due to the decrease in $NO_2$ concentration or to the increase in relative humidity. If a concomitant peak shift and intensity variation is observed, it is due to the presence of humidity. If no peak shift is observed, the variation must be ascribed to $NO_2$ concentration variations. The same discrimination can be obtained with ethanol. An appropriate pattern recognition step could improve preliminary results of gas species identification and quantification.

## Conclusions

We have shown that in a porous silicon microcavity, the photoluminescence intensity, the electrical conduction, and the resonance peak of the cavity are affected by the presence of $NO_2$, ethanol, and water in a different way. Thus, the use of porous silicon as multiparametric sensors can help to discriminate the presence of $NO_2$, which is a dangerous pollutant, from interferent gases like humidity and ethanol.

$NO_2$ increases DC current and PL intensity, but no peak shift is produced. Humidity and ethanol causes a peak shift and decrease in DC current. The peak shift is higher with ethanol than with water due to the higher value of refractive index, while the conductance decrease is higher with humidity than with ethanol. In contrast with the case of nitrogen dioxide, the peak intensity variation is small for both humidity and ethanol.

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*Sample Availability:* Available from the author.