

## Multiparametric porous silicon gas sensors with improved quality and sensitivity

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We have fabricated a multiparametric gas sensor based on porous silicon. The sensing parameters are the electrical conductivity of a single porous Si layer and the resonance wavelength of a porous silicon microcavity, both fabricated on the same substrate. The electrical conductivity allows detection of 50 ppb of nitrogen dioxide in dry air. Although relative humidity also affects the electrical conductivity, the contributions due to nitrogen dioxide and to humidity can be distinguished by simultaneously monitoring the cavity resonance wavelength and the current. We also demonstrate a three-contact configuration which further increases the sensitivity of the electrical response of the sensor.

**1 Introduction** Electrical conductivity, photoluminescence (PL) and effective refractive index of porous silicon (PSi) are sensitive to the presence of different gases [1, 2]. Since they depend on different physical properties of the gas, the simultaneous monitoring of all three parameters gives independent information about the gas. For example, a strong correlation between the PL intensity and the static dipole moment of gas molecules has been demonstrated. The refractive index of the gas, and thus of the PSi, depends on the other hand on the dynamic response of the gas molecules at optical frequencies [3]. Therefore, having access to several gas properties, multiparametric PSi sensors are expected to have better gas selectivity than single parameter PSi sensors.

In this work, we study the multiparametric strategy applied to pollutant detection. We focus on NO<sub>2</sub> detection because NO<sub>2</sub> quite often exceeds attention levels in urban areas, and on the other hand the electrical conductivity of PSi is known to be very sensitive to the presence of NO<sub>2</sub> [4]. The latter fact motivates the choice of the electrical conductivity as first parameter for the sensor proposed in this work. The required sensitivity to NO<sub>2</sub> for pollution detection is at least 100 ppb [5]. In our sensor, we demonstrate a 50 ppb level detection using the DC electrical conductivity, and also a three electrode configuration which can further improve sensitivity.

We show below that realistic humidity levels affect the PSi resistivity to an extent which is comparable to the effect of realistic NO<sub>2</sub> concentrations. Unfortunately, both water and NO<sub>2</sub> are normally present in atmosphere. Hence, the electrical conductivity cannot be associated univocally to the concentration level of NO<sub>2</sub>. The multiparametric strategy here proposed precisely addresses this issue. We propose the refractive index as the second parameter. NO<sub>2</sub> is not expected to affect the refractive index of air because

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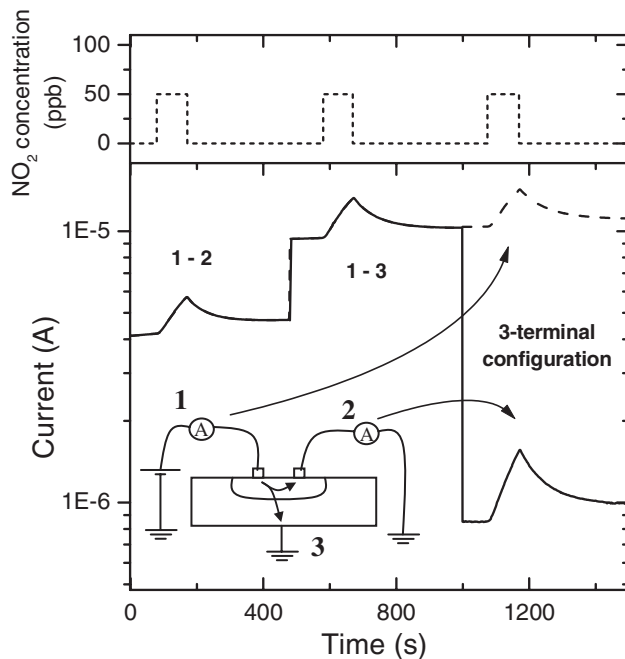
of its low concentration in realistic atmospheric conditions.[1] We prove here, using a Fabry-Perot PSi optical microcavity (PSM), that water vapor can easily be identified through a change of the refractive index of PSi layers, whereas no comparable change is caused by  $\text{NO}_2$ . The observation of a shift of the reflectance spectrum due to water vapor implies a certain degree of water condensation inside the pores because the refractive index of humid air does not explain the quantitative shift of the resonance. The fact that both the humidity and  $\text{NO}_2$  similarly affect the electrical conductivity, whereas the resonance significantly shifts only under humidity changes, demonstrates that both parameters provide independent information, and strongly supports the multiparametric strategy.

**2 Experiments and discussion** Samples were prepared using p-type highly doped Si substrates ( $\rho = 0.01 \Omega \text{ cm}$ ). On the same substrate type, the multiparametric sensor was composed by both a single layer with moderate porosity (65%) for the electrical conductivity monitoring, and by a PSM for the reflectivity measurements. This separate configuration allows independent optimization of the electrical and the optical sensitivity, and avoids that the light required by the reflectivity measurement affects the electrical measurement.

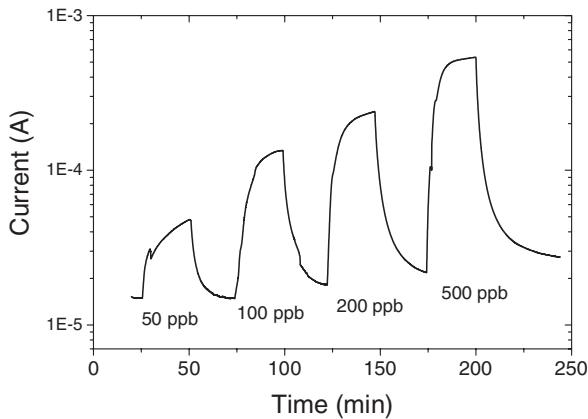
The single PSi layer was fabricated using an electrochemical solution obtained mixing a 48% aqueous HF solution with ethanol in a volumetric ratio 1:2, and applying a  $50 \text{ mA/cm}^2$  anodization current density, for 136 s or 1360 s to have  $3 \mu\text{m}$  or  $30 \mu\text{m}$  thickness, respectively. Two thick gold electrodes were evaporated on the top PSi-air interface.

The PSMs were fabricated using a well known procedure, [6] as two facing Distributed Bragg Reflectors (DBRs) separated by a spacer of  $\lambda/2$  optical thickness ( $\lambda$  is the cavity resonance wavelength). The DBRs were fabricated as stack of 6 periods, each period being a set of 2 layers, a high porosity  $\lambda/4$  layer ( $50 \text{ mA/cm}^2$  current density, 65% porosity) and a low porosity  $\lambda/4$  layer ( $5.75 \text{ mA/cm}^2$  current density, 45% porosity).

Samples were mounted inside an air-tight gas flow chamber and contacts were wired. The reflectivity measurements were performed using light coming from a commercial halogen light bulb, coupled to a microscope and passing through a quartz window in the gas chamber. Gases diluted in dry air came from certified bottles; they were mixed by MKS flow-meters and sent to the chamber at room temperature. Relative humidity and temperature were constantly monitored by a commercial sensor.



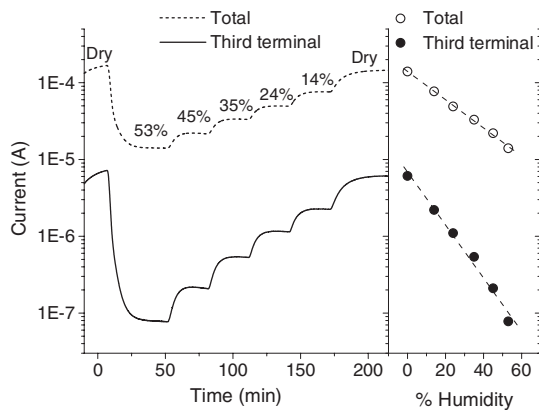
**Fig. 1** Electrical response to three short exposures to 50 ppb of  $\text{NO}_2$  in dry air with different measuring configurations. First exposure: total electrical current biasing between terminals 1 and 2 with 3 floating. Second exposure: total electrical current biasing between terminals 1 and 3 with 2 floating. Third exposure: currents measured in the three-terminal configuration shown in the inset diagram. The dashed line shows the total current (terminal 1) and the solid line shows the current measured through terminal 2. The bias voltage was 100 mV.



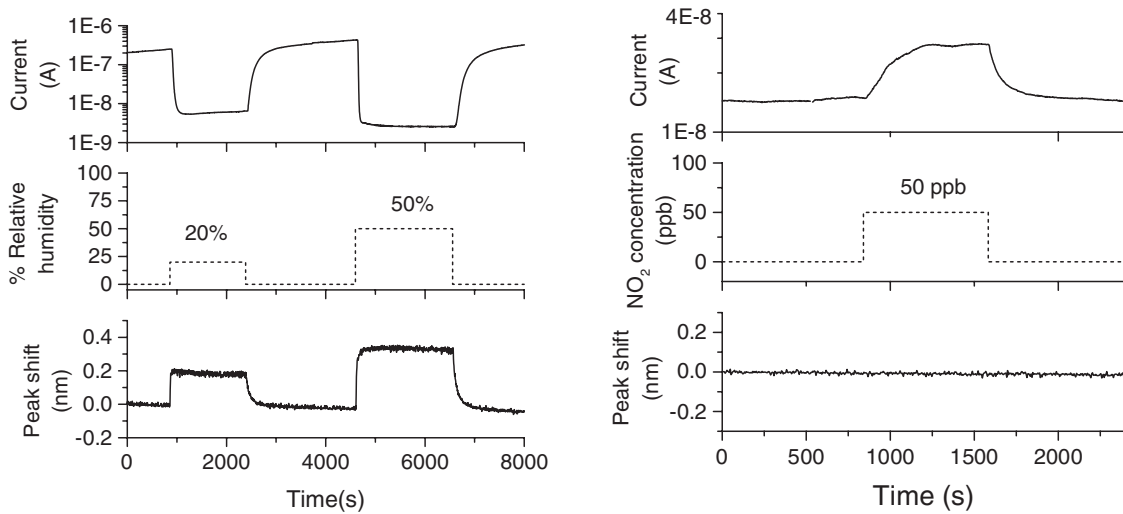
**Fig. 2** Total current with a bias voltage of 100 mV applied between one electrode and the substrate of the 30  $\mu\text{m}$  PSi monolayer. The plot shows the response to the intermittent exposure to different  $\text{NO}_2$  concentrations in dry air.

The required sensitivity in the electrical conductivity of PSi (at least 100 ppb) is not trivially achievable. Elaborated pre-anodization steps have been successfully suggested to highly improve the sensitivity towards this goal [5]. In this work, we propose an alternative solution which does not require any additional process beside the usual anodization step. The idea is schematically shown in Fig. 1 (at bottom-left) and requires two electrical contacts in the top PSi-air interface (wires 1 and 2) and a contact on the substrate (wire 3). Instead of applying a voltage bias between contacts 1 and 3 (contact 2 floating) or between 1 and 2 (contact 3 floating), and reading the current output by the voltage source, as usually done, we propose to apply the voltage between contact 1 and 3 and to read the current through an ammeter connecting contact 2 and 3. For a given variation in the gas composition, a larger relative variation of the current – thus a larger sensitivity – is observed in the latter case. The reason is that in both former configurations the current always crosses the PSi layer in vertical paths, whereas in the latter case the substrate (contact 3) and the contact 2 are at the same voltage. Thus the resistive current injection between contacts 2 and 3 is inhibited in the latter case and the current in 2 is essentially injected directly by contact 1 only.

It is interesting that data of Fig. 1 actually refer to measurements performed using a 50 ppb  $\text{NO}_2$  concentration in air. Indeed, we have been able to perform complete sets of meaningful measurements of  $\text{NO}_2$  in dry air at different concentrations without resorting to the three-terminal configuration. Figure 2 shows the effect of  $\text{NO}_2$  on the total current flowing through contact 1. Despite this, our understanding is that the three terminal configuration might be essential in real applications, since our preliminary results with mixtures of  $\text{NO}_2$  and water vapor (not reported here) seem to indicate that humidity quenches the sensitivity of PSi to  $\text{NO}_2$  when a simple two electrode configuration is used.



**Fig. 3** Electrical current response to humidity measured on the 3  $\mu\text{m}$  sample employing the three-terminal configuration. Left plot: temporal response applying different humidity percents. The dotted and the solid line represent the total and the third-terminal currents respectively. Right plot: steady-state currents with respect to humidity percents. The white and black dots represent the total and the third-terminal currents respectively.



**Fig. 4** Simultaneous measurement of optical and electrical response to humidity and NO<sub>2</sub>. The electrical current is measured on the 30  $\mu$ m deep monolayer employing the three-terminal configuration, and the reflectance peak shift is measured on the microcavity. Left plot: response to two different humidity values in absence of NO<sub>2</sub>. Right plot: response to 50 ppb of NO<sub>2</sub> in presence of 20% humid air.

The usefulness of the three-terminal configuration is clearly demonstrated in Fig. 3. In the left graph, both the total current (ammeter of contact 1) and the third-terminal current (ammeter of contact 2) are reported during relative humidity variations. The graph clearly shows that the relative variations of the third-terminal current are significantly larger. For example, the first change from dry air to 50% relative humidity induces a drop of one order of magnitude in the total current whereas the drop is by two orders in the third terminal. On the same y-scale, the right plot reports the steady-state current levels as functions of the relative humidity for both currents. The better sensitivity of the third-terminal current is shown by the steeper slope of the linear fit of the experimental points. It should be noticed that the overall dependence of the current on the relative humidity is actually exponential, since the y-scale is logarithmic.

Despite the encouraging result shown in Fig. 2, NO<sub>2</sub> detection cannot be based on the electrical conductivity alone, as the following facts indicate. Considering the relative humidity alone, a variation from 50% to 40% should be considered possible during a time span, say, of one day. The relative variation of the total current (contact 1) associated to such change is about a factor 2 (from the hollow circles and their linear fit, Fig. 3). Figure 2 shows that in our sensor the same amount of relative variation appears when the concentration of NO<sub>2</sub> (in dry air) changes from 100 ppb to 200 ppb (approximately the attention and the alarm level respectively according to Italian legislation). This indicates that the single parameter PSi sensor (parameter: electrical conductivity) has no capability to distinguish between the two situations.

For what above discussed, we have fabricated a PSM on the same substrate type, in order to detect changes of the resonance wavelength consequent to changes of the refractive index of the gas [1, 3, 7]. The resonant wavelength has been monitored measuring the PSM reflectivity, which is close to 100% over the whole PSM stop-band except at the resonance [6]. Figure 4 shows the response of both parameters to changes in humidity and in NO<sub>2</sub> independently. We can appreciate that humidity quenches the electrical signal and red-shifts the reflectance peak. However, NO<sub>2</sub> only leads to electrical response, as we do not observe any peak-shift. This fact allows us to conclude that, since the resonance shifts can be only associated to the presence of water vapor, a calibration of the electrical response for different humidity values would allow to calculate the NO<sub>2</sub> concentration under any condition of humidity.

**3 Conclusions** We have shown that a porous silicon gas sensor based on electrical conductivity does not distinguish between low NO<sub>2</sub> concentrations and different humidity conditions. Therefore, a specific PSi sensor requires simultaneous monitoring of another parameter, and our proposal is the index of refraction by means of the peak position of reflectance of a PSM. We demonstrate that these two parameters are independent, thus NO<sub>2</sub> and humidity are separable. We also propose an electrical configuration based on three contacts that increases the sensitivity of the electrical measurement. Our multiparametric sensor has at least the required sensitivity to detect 50 ppb of NO<sub>2</sub>, both in dry air and in 20% relative humidity.

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