

Improved reversibility in aged porous silicon NO₂ sensors

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Abstract

Porous silicon (PS) conductometric gas sensors can exhibit large sensitivity to gases, due to the large surface versus volume ratio of porous silicon. A possible application is the detection of traces of nitrogen dioxide (NO₂), an air pollutant. $\Delta G/G$ signals in excess of 10 in the presence of concentrations as low as 50 ppb in dry air can be demonstrated. Unfortunately, such high sensitivity to NO₂ is achieved, in fresh samples, with poor reversibility. Another problem is the interference of water vapor, which also affects the porous silicon conductivity. However, we show that reversibility is complete in aged samples, and sensitivity to water vapor is lowered. Although in aged samples large $\Delta G/G$ signals are harder to achieve, we show that concentration levels of NO₂ at few tens of ppb are still detectable.
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1. Introduction

Electrochemical anodization of silicon substrates results in so-called porous silicon (PS), a “quantum sponge” structure with pores diameters ranging from few nanometers up to some micrometers, depending on the fabrication [1]. The internal surface/volume ratio of PS is typically of the order of 500 m²/cm³ [1]. This large value accounts for the enhanced reactivity of PS layers in contact with several chemical species. This feature is an advantage if PS is exploited as a sensing material [2]. Liquids or gases penetrating into the pores can affect several physical properties of PS. One of these sensitive properties is the electrical conductivity of the porous layer. Devices exploiting conductivity as transduction mechanism, i.e. conductometric PS sensors—have been demonstrated, for example, for HCl, NH₃ and NO [3], for humidity [4,5], for organic molecules [2] and ethanol [6]. The appealing characteristics of these PS sensors are low cost, room temperature operation and possibility of integration with electronic circuits [7].

Nitrogen dioxide (NO₂) is a toxic air pollutant emitted by combustion engines. The attention level of NO₂ in air

is about 100 ppb [8].¹ The control of NO₂ concentration in urban areas has become increasingly important, but unfortunately cheap solid-state sensors for detecting low levels of NO₂ are not available yet. Recently, NO₂ sensors based on PS have been developed, which can detect concentrations of NO₂ in air near and even below the attention level [9–12]. In [12], Pancheri et al. have proposed a PS sensor, which can detect NO₂ at 50 ppb level at any relative humidity (RH) between 0 and 70%, thus demonstrating that the necessary sensitivity for NO₂ pollution monitoring is achievable.

Unfortunately, it is not possible to use the device of [12] for practical applications. The first difficulty is the effect of relative humidity on conductivity. For example, a switch from 40% RH to dry air, without introducing NO₂, leads to a conductance increase of around one order of magnitude, which is about half of the change obtained adding 50 ppb of NO₂ without changing the RH (kept at 40%) [12]. Clearly, such behavior is undesirable, since the conductometric measurement alone cannot distinguish between variations associated to changes of RH and of NO₂ concentration.

The second issue is the reversibility. The exposure to NO₂ at 50 ppb for 30 min leads to a 35% irreversible increase of the sensor baseline conductance, i.e. the conductance in the absence of NO₂. This shift is associated to a partial pollution

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¹ For example, Italian legislation fixes an attention level for the concentration of this gas at 106 ppb and an alarm level at 212 ppb.

of the sensor. By comparing to this shift the useful signal (i.e. the $\Delta G/G$ associated to the presence of NO_2), one realizes that the useful signal (at 50 ppb level) is less than ten times this baseline shift [12]. It can be inferred that longer but realistic exposure to NO_2 are likely to cause baseline shifts comparable to the useful $\Delta G/G$ signal. This situation is of course seriously compromising any use of the sensor for the proposed application.

In order to attack the above two problems, we have considered tests on aged samples. The starting idea has been to investigate the effect of the spontaneous oxidation of porous surface, under the expectation that the native oxide could act as a passivating layer, thus possibly leading to more reversible—although less sensitive—devices. In this work, we show that aging has this passivating effect. An interesting additional feature is the quenching, in aged samples, of the effect of RH on conductance. Both results suggest that PS surface passivation by oxidation might be an effective way to obtain reversible and moisture-insensitive sensors.

2. Experimental

Meso-porous silicon layers were grown by electrochemical dissolution in an HF-based solution on a single-crystalline p^+ -type silicon substrate. Substrate resistivity was between 0.006 and 0.015 $\Omega \text{ cm}$. Before the anodization, the native oxide was removed from the backside of the wafers, and aluminum back contacts were deposited by evaporation. The anodizing solution was obtained by mixing a 30% volumetric fraction of aqueous HF (48 wt.%) with ethanol. We applied an etching current density of 50 mA/cm^2 . We fabricated two types of samples. The first type (hereafter called A) was fabricated using an etching time of 23 min, whereas the second type (B) was obtained with an etching time of 127 s. After anodization, the samples were rinsed in ethanol and pentane, and dried in ambient air. SEM micrographs show a layer depth of 32 μm for type A, and about 3 μm for type B. Normal reflectance measurements give a refractive index of about 1.4 for both types of samples. Using Bruggeman approximation [5] we have estimated that porosity was about 80%. On each sample, a few gold electrodes were deposited by evaporation on the PS top surface. Copper wires were connected to the gold electrodes using an epoxy silver paste.

During measurements in the presence of NO_2 and water vapor, the sensors were biased between one of the top contacts and the back contact at a constant voltage, while the current was measured. The sensors were kept in a sealed chamber under controlled flux of gases coming from certified cylinders. Humid air was obtained by flowing dry air through a bubbler. Different relative humidity levels and NO_2 concentrations were obtained mixing humid air, dry air and a dilute solution of NO_2 in air (550 ppb) with a flow control system. Relative humidity was monitored using a calibrated hygrometer.

Measurements were done on as prepared (hereafter referred to as fresh) and on aged samples.

3. Results

We started fabricating sensors with type A samples, since they are known to give highly sensitive NO_2 sensors [12]. In Fig. 1, we report the effect of sample aging on the sensitivity of such type A sensors to water vapor. Samples were dc biased at +1 V on the top electrode while the current flow was monitored. Current measurements in Fig. 1 are shown as conductance ($G = I/V$). In fresh samples (solid squares in Fig. 1), G decreases with increasing relative humidity, as expected [12]. We measured a decrease of G of about an order of magnitude by changing the RH from 27 to 67%. However, after using such samples for our tests with vapor and NO_2 for a few days, the sensitivity to different levels of RH decreases, and almost disappears after 10 days (solid circles, Fig. 1). After the first 10 days, the samples were kept in non-sealed containers and periodically measured (e.g. after 25 and 75 days, solid triangles, Fig. 1). The fact that the curve after 10 days is above the 25 and 75 days curves could be due to the exposure to NO_2 tests, and suggests that in the long term the sensor pollution with NO_2 might be at least partially reversible. Saturation of aging is observed in Fig. 1 after 25 days. The results shown in Fig. 1 point out that aging leads to insensitivity to water vapor, and encouraged further investigation on sample aging.

In our following study, we concentrated on type B samples (thickness: 3 μm), because aging (i.e. oxidation) reduces samples conductivity, and the starting conductivity of type B is significantly larger than that of type A. By applying a positive bias to the bulk silicon electrode and grounding the electrode on PS, we achieved current values of some tens of microamperes. Current values above the

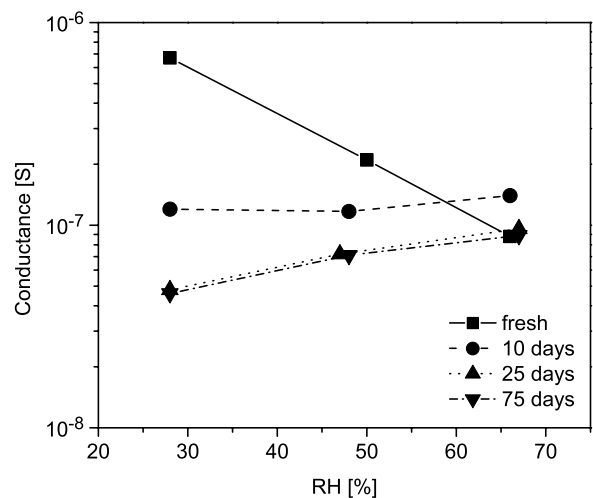


Fig. 1. Effect of relative humidity on electrical conductivity of fresh and aged type A PS samples. The thickness of the porous layer is 32 μm .

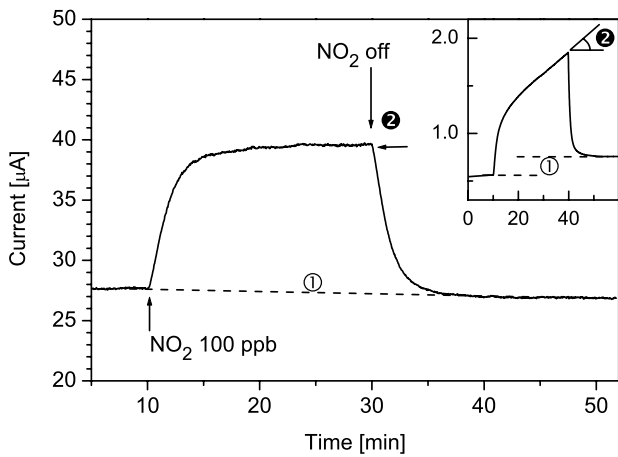


Fig. 2. Effect of exposure to NO₂ (concentration of NO₂: 100 ppb) on thin (3 μm) aged samples (main plot) and on thick fresh samples (inset). Relative humidity is 30% in both cases. Temperature is 22 °C. The baseline shift (1) is absent in the aged sample and significant in the fresh sample, and the signal stabilization (2) is good in the aged thin sample and poor in fresh thick sample.

microamperes range are desirable for noise and cross-talk immunity. In Fig. 2, we report a typical measurement—on an aged sample of type B (3 months)—of the effect of NO₂ (at 100 ppb) in 30% RH.

Fig. 2 shows some remarkable features. A first feature is the total absence of an upward shift of the baseline after the NO₂ exposure (1 in Fig. 2, main plot). By careful looking, one could actually notice that there is a very slight trend downwards, whose origin is still not known. Such trend was present also before the NO₂ exposure. The result suggests that exposure to NO₂ has improved reversibility in this sensor. In all fresh samples we have tested, on the contrary, an upward baseline shift is always measured after the exposure to NO₂ (1 in Fig. 2 (inset), shows the effect of NO₂, during the same measurement, on a fresh sample of type A). A second feature of Fig. 2 is the settling of the current to a rather stable level (about 40 μA) after insertion of NO₂ into the gas flow (2 in Fig. 2, main plot). This results also contrasts with results obtained in fresh samples, in which the current is not settled even after 30 min (2 in Fig. 2 (inset)).

Finally, we have repeatedly tested type B samples applying timed sequences of mixed gas flows, composed by synthetic air, water vapor and NO₂ at different concentrations. A typical snapshot of one of our measurements is shown in Fig. 3. Data in Fig. 3 were obtained by applying four times a 5 min exposure to NO₂-containing humid air (RH: 30%). Each time, a different concentration of NO₂ was applied (100, 80, 60, and 40 ppb, respectively), followed by a 5 min recovery period (humid air containing no NO₂).

We have chosen 5 min exposure cycles on the basis of Fig. 2, which shows that, after the insertion of NO₂, in 5 min the signal reaches 90% of the settled value after 30 min. Although the final value is not totally settled in 5 min, such

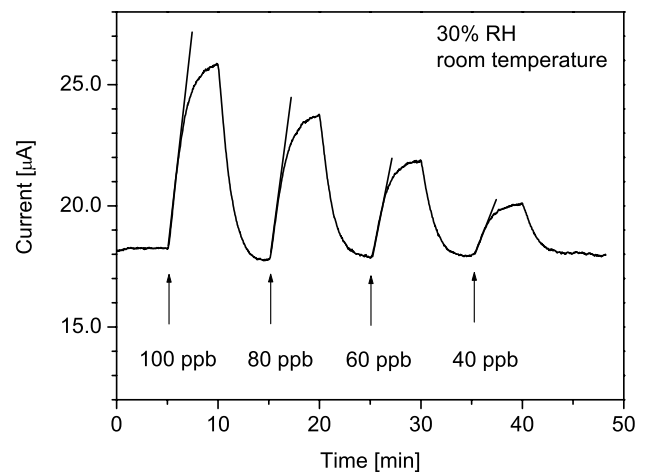


Fig. 3. Effect on PS resistivity due to exposure to different levels of NO₂ in a thin (3 μm) aged sample. Similarly to what seen in the aged sample of Fig. 2, we observed good baseline recovery after each NO₂ pulse.

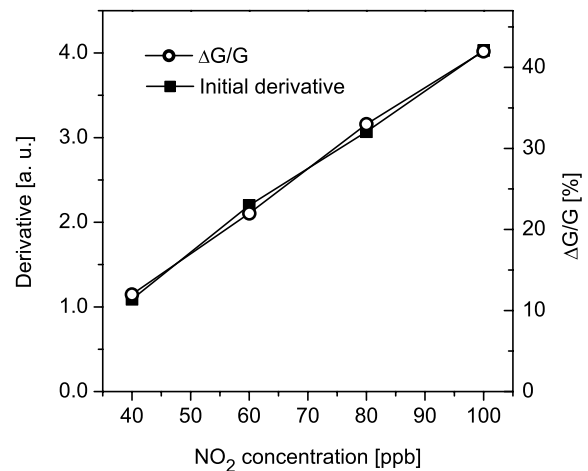


Fig. 4. Relative conductivity variation after 5 min of exposure to NO₂ ($\Delta G/G$, open circles), its initial (solid squares) time derivative, of thin (3 μm) aged PS samples, as a function of NO₂ concentration.

fast cycles allowed quick yet complete characterizations in less than 1 h. We have found that this was a good compromise, which completely avoided long-term fluctuations due to temperature changes. From data in Fig. 3, we have extracted the ΔG associated to 5 min exposures, the initial derivative dG/dt (right after the NO₂ insertion) as the slope of the lines in Fig. 3. The dependence of these quantities on NO₂ concentration is reported in Fig. 4. As can be seen in the diagram, both the relative change ($\Delta G/G$) and its initial derivative show excellent linearity with respect to the NO₂ concentration.

4. Conclusions

We have shown that in aged PS samples, the changes in resistivity of the porous layer, associated to exposure to NO₂

(at 40, 60, 80 and 100 ppb concentration) have improved reversibility compared to fresh samples. The stabilization of the current is also faster in aged than in fresh samples. Both results suggest that sample aging is a potentially good strategy for use of PS in NO₂ conductometric sensors, since reversibility and signal stabilization are still major unsolved limitations for such applications in freshly etched PS sensors. Further efforts should be made to develop an oxidation treatment which could reproduce the effects of aging on PS conductivity, in order to achieve the good performance obtained for aged sensors with a controllable technological treatment.

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