

Letter to the Editor

Very sensitive porous silicon NO₂ sensor

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Abstract

We report a nitrogen dioxide sensor suitable for environmental control, based on the change in conductivity of a single meso-porous silicon (PS) layer with about 80% porosity. We present the characterization of the sensor in the presence of low concentrations of NO₂ in dry air and study the influence of humidity on sensor behaviour. The sensor shows a sensitivity to 12 ppb of NO₂ in dry air and a good response to 50 ppb in humid air.

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1. Introduction

Nitrogen dioxide (NO₂) is a toxic air pollutant emitted by combustion engines. Italian legislation fixes an attention level for the concentration of this gas at 106 ppb and an alarm level at 212 ppb [1]. While the control of NO₂ concentrations in urban areas has become increasingly important, inexpensive solid-state sensors for detecting low levels of NO₂ are currently unavailable. Recently, NO₂ sensors based on porous silicon have been developed to detect concentrations of NO₂ in air near the attention level [2,3]. Advantages of porous silicon sensors are low cost, room temperature operation and possible integration with electronic circuits [4].

In this work, we present a NO₂ sensor based on the conductivity variation of a meso-porous silicon (PS) layer. A dc electrical characterization was performed under different NO₂ concentrations and relative humidity (RH) levels.

2. Experiment

A meso-porous silicon layer was 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 Ω cm. Before the anodization, the native oxide was

removed from the backside of the wafer, and an aluminium back contact was 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/cm² for 23 min. The sample was rinsed in ethanol and pentane, and was dried in ambient air. SEM micrographs show a layer depth of 32 μm, and normal reflectance measurements give a refractive index of about 1.4. Using Bruggeman approximation [5] we have estimated that porosity was about 80%. Gold electrodes were deposited by evaporation on the porous silicon's top surface. Copper wires were connected to the gold electrodes using an epoxy silver paste.

The sensor was biased between one of the top contacts and the back contact at a constant voltage (1 V) while the current was measured. During the measurements, the sensor was kept in a sealed chamber under a controlled flux of gases coming from certified cylinders. Humid air was obtained by flowing dry air through a bubbler. Different relative humidity levels and NO₂ concentrations were obtained mixing humid air, dry air and a dilute solution of NO₂ in air (550 ppb) with a flow control system. Relative humidity was monitored using a calibrated hygrometer. Measurements were done within 1 month of the fabrication of the sample.

3. Results and discussion

Fig. 1 shows the dynamic response of the sensor versus the concentration of NO₂ in dry air from 240 down to 12 ppb at

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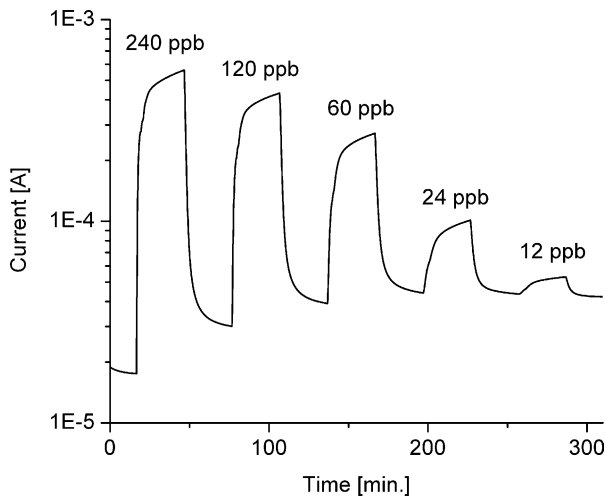


Fig. 1. Dynamic response of the sensor to different concentrations of NO_2 in dry air.

room temperature (24°C). The sensor shows a very high sensitivity: an increase in the current can be seen even at NO_2 concentration as low as 12 ppb with a ratio $\Delta G/G$ of 0.26.

An increase in the current baseline can be observed in Fig. 1. Preliminary recovery tests (not shown) suggest that the baseline shift is at least partially reversible once the sample is kept in clean air for several hours. However, the recovery appears to be incomplete, possibly indicating an irreversible interaction of NO_2 molecules with porous silicon's internal surface. This interpretation is consistent with the known effect of irreversible quenching of PS photoluminescence in the presence of NO_2 [6]. The reversibility is clearly a crucial question which must be addressed.

Fig. 1 shows that sensor response and recovery time constants are of the order of 10 min, but there is not a complete stabilization even after 30 min.

The influence of NO_2 on meso-PS has been recently studied measuring IR-absorption and conductivity variations [7,8] and a model for the interaction of NO_2 with meso-PS has been proposed. The molecules of NO_2 act as acceptor centres. Once they have been adsorbed on PS surface, the acceptor-like character would lead to an increase of free carrier (holes) concentration thus explaining the increase in conductivity.

Fig. 2 shows sensor response and recovery applying 50 ppb of NO_2 at different RH levels. Sensor current depends strongly on the relative humidity. An increase in RH leads to a decrease in conductivity and therefore, in sensor current. The observed behaviour could be qualitatively explained with a donor-like character of water molecules adsorbed at PS surface defects [8]. Their effect would be a lowering of the free holes concentration.

The relative change of conductivity $\Delta G/G$ in the presence of NO_2 (50 ppb) decreases with increasing relative humidity, passing from 11.7 for 0% RH, to 2.2 for 40% RH, to 1.2 for

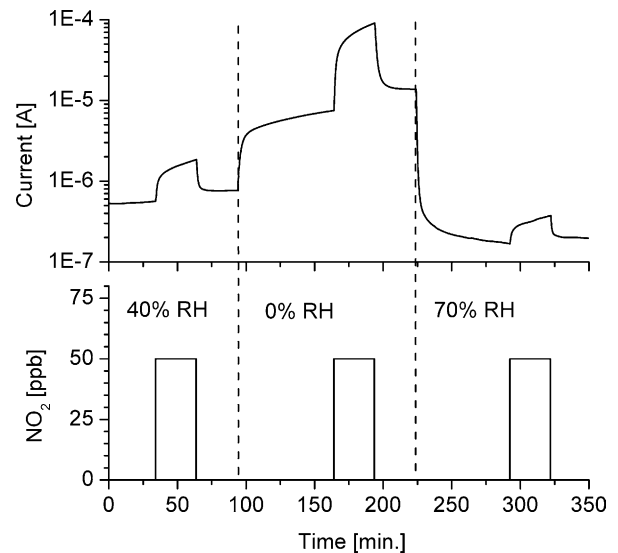


Fig. 2. Dynamic response of the sensor in the presence of different relative humidity levels and NO_2 concentrations. The graph above represents the sensor response, the graph below represents NO_2 concentration as a function of time. The dashed vertical lines divide regions with different relative humidity values.

70% RH. The relevant fact of Fig. 2 is that the sensitivity to 50 ppb of NO_2 is measurable even in the presence of humidity rates typical of ambient air. The decrease in sensitivity could be due to a partial compensation effect between the acceptor-like NO_2 molecules and the donor-like water molecules. A low cost strategy to separately quantify the effect of RH and NO_2 could be a simultaneous monitoring of the effective index of refraction of the porous layer, which depends on the water content inside the porous layer, but not on the NO_2 concentration [9].

4. Conclusions

A very sensitive meso-PS NO_2 sensor was presented, which can detect very low concentrations of NO_2 in the presence of different RH levels at room temperature. The sensitivity to NO_2 decreases with increasing relative humidity, but it remains sufficiently high for an application of the sensor in the field of environmental monitoring.

Since the sensor signal also responds to ambient humidity, quantitative NO_2 detection requires an independent measurement of the ambient humidity. Preliminary tests indicate that the effect is not completely reversible.

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