

Opposite effects of NO₂ on electrical injection in porous silicon gas sensors

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(Received 17 November 2003; accepted 1 April 2004; published online 12 May 2004)

The electrical conductance of porous silicon fabricated with heavily doped *p*-type silicon is very sensitive to NO₂. We show that the sign of the injection variations depends on the porous layer thickness. If the thickness is sufficiently low—of the order of few μm —the injection decreases instead of increasing. We discuss the effect in terms of an already proposed twofold action of NO₂, according to which the free carrier density increases, and simultaneously the energy bands are bent at the porous silicon surface. © 2004 American Institute of Physics. [DOI: 10.1063/1.1757025]

Porous silicon (PSi) is obtained by electrical anodization of crystalline silicon (Si) substrates.¹ It has received much attention after the discovery of efficient room temperature photoluminescence.² Recent reviews are available.^{3,4} The internal surface to volume ratio of PSi can reach several hundreds of m^2 per cm^3 , leading to strong dependence of optical and electrical properties of PSi on the environment. For this reason, PSi is an interesting material for gas sensors.⁵

Recently, several reports have focused on PSi sensors fabricated using heavily doped *p*-type Si (*p*⁺ PSi), in which the sensitive parameter is the electrical conductance.^{6–11} In absence of gases, the electrical injection in sufficiently thick ($\approx 30 \mu\text{m}$) *p*⁺ PSi layers is very low. In fact, anodization leads to a porous structure almost depleted of mobile charges. However, the concentration of boron dopants is essentially unchanged by the anodization, remaining approximately as high as in the starting *p*⁺ substrate ($\approx 10^{19} \text{cm}^{-3}$).^{12,13} The absence of mobile charges is ascribed to hole trapping,⁸ but the actual mechanism is still controversial.¹¹ In presence of specific gases, the mobile carrier population changes, usually leading to increases of conductance, as in the case of NO₂ (Refs. 6–11) or NH₃.¹¹

The presence of NO₂ is reported to free the trapped holes at interface states.^{8,9} As a consequence, the conductivity increases with the increased free hole concentration.^{6–10} The process is very effective for sensing: the presence of NO₂ can be detected at concentrations as low as 12 ppb.¹⁰ NO₂ is a by-product of internal combustion engines and can cause lung diseases. Most pollution regulations set the warning level of NO₂ around 100 ppb (for example, Italian Ministerial Decree, 15 April 1994). Hence, the required level of sensitivity for realistic applications is attainable in *p*⁺ PSi.

The sensitivity to NO₂ is affected by both sensor's porosity⁶ and micro structure.¹⁴ In this work, we report a quite surprising effect: the electrical injection in *p*⁺ PSi in presence of NO₂ can increase or decrease, depending on the thickness of the *p*⁺ PSi layer. The known effect—the in-

crease in the electrical injection caused by the increase of conductance—has been reported in *thick* samples ($\approx 30 \mu\text{m}$).^{6–10} We report here for the first time the opposite behavior in *thin* samples ($\approx 2 \mu\text{m}$), in which the injection *decreases* in presence of NO₂.

p⁺ PSi layers were grown by electrochemical dissolution in an HF-based solution on a single-crystalline *p*-type (100) heavily-doped Si substrate. Substrate nominal resistivity ρ was 6–15 $\text{m}\Omega \text{cm}$. Before anodization, the native oxide was removed from the back side of the wafers, and aluminum back contacts were deposited by evaporation. In order to achieve high sensitivity to NO₂, we have used an anodizing solution consisting of a mixture of 3 parts (in volume) of aqueous HF (48% wt.) and 7 parts of ethanol. The etching was performed by applying an etching current density of 50 mA/cm^2 . We fabricated two types of samples. The first type (hereafter referred to as “thick”) was fabricated using an etching time of 1363 s, whereas the second type (“thin”) was obtained with an etching time of 127 s. Thus, thick and thin samples were fabricated by using exactly the same procedure, except for the anodization time. After anodization, the samples were rinsed in ethanol and pentane, and dried in ambient air. Scanning electron microscopy images showed a layer thickness of about 32 and 2 μm , respectively, for thick and thin samples. From normal reflectance measurements, a refractive index of about 1.4 was calculated, and using Bruggeman approximation⁴ we have estimated that porosity was about 78%.

Gold electrodes were deposited by evaporation on the PSi top surface. Copper wires were connected to the gold electrodes using an epoxy silver paste.

For the electrical characterization, 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 NO₂ concentrations were obtained by 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. In order to characterize the time response, a bias voltage of -1 V was applied on one of the

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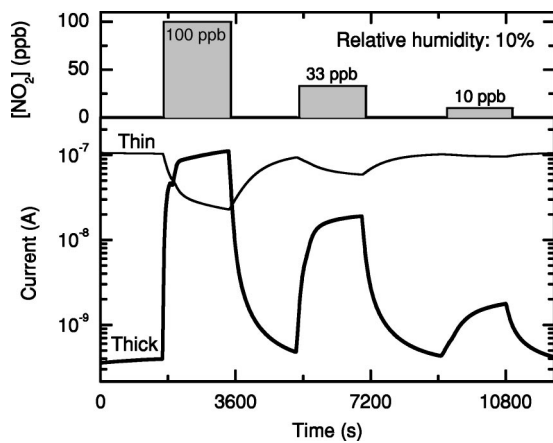


FIG. 1. Simultaneous measurement of current injection in thick and thin sensors, under fixed bias voltage (bottom plot) and under controlled gas flux as a function of time. The bias voltage was -1 V applied to one of the top contacts with respect to the back contact, for both sensors. The dynamics of the sensors is not limited by the setup, whose time response is about 1 min. The kink at 1800 s is probably due to a small gas fluctuation. The top plot shows the composition of the gas flux.

top contacts with respect to the back contact, and the injected current was constantly monitored (Fig. 1). Although the injected current does not totally stabilize after 30 min, Fig. 1 suggests that most significant current variations are observed within such time period. Thus, $I-V$ characterization, performed as a separate measurement, was acquired after waiting 1800 s (the assumed settling time required from the activation of the gas switch). $I-V$ characterizations are reported in Fig. 2.

The main result discussed in this work is clearly visible in both Figs. 1 and 2: in presence of NO_2 , the injected current increases in the thick sensor, and decreases in the thin one.

In the case of the thick sensor, the impedance of the device is dominated by the high resistance of the thick central layer. During the exposure to NO_2 , the conductance of the p^+ PSi layer increases, as a consequence of the release of trapped holes, as already established.^{8,9} Thus, the injection increases in presence of NO_2 . In Fig. 2, the increase is visible by comparing the thick lines of plots (a) and (b). The $I-V$ characteristic is symmetric with respect to a change in the sign of the voltage.

The behavior of the thin sensor is harder to explain. The

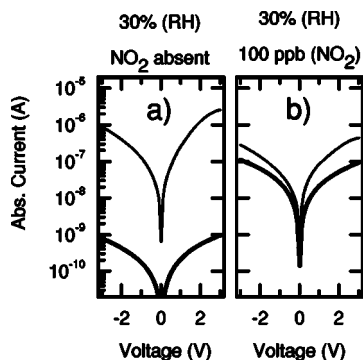


FIG. 2. dc electrical characteristics of thick (thick line) and thin (thin line) sensors. The voltage sign is positive on the top contact with respect to the back. The composition of the gas flux is reported on top of each plot (RH = relative humidity).

first observation is that in absence of NO_2 the current injection is three orders of magnitude larger than in the thick sensor [Fig. 2(a)], even though the thickness is only one order of magnitude lower. This suggests that, in the thin sensor, the current injection is limited by the junctions rather than the resistivity of the porous layer.

The value of the work function of gold is similar to the work function of p^+ Si ($\phi_{\text{Au}} \approx 5.1$ eV). Therefore, we assume that the two junctions behave similarly, in terms of the balance of excess charge at the junction regions. Since the p^+ PSi is essentially an intrinsic semiconductor,^{12,13} the dc electrical current versus voltage characteristic should be similar to the one of a quasi-symmetric p^+-i-p^+ device. Although this is clearly a rough simplification, it is experimentally justified by the almost symmetrical the $I-V$ characteristics of the thin sensor (Fig. 2).

In n^+-i-n^+ Si structures, when the distance between the junctions is in the range of $2 \mu\text{m}$ or less, extra free carriers diffusing from the heavily doped regions accumulate over the whole intrinsic region.¹⁵ Since the doping profiles of Ref. 15 are comparable to our equivalent p^+-i-p^+ structure, we similarly expect that the hole density in the whole porous layer of our thin sensor will be larger than the equilibrium density in bulk p^+ PSi.

Also, the injection is largely affected by the distribution of defect states inside the energy gap.¹⁵ This latter fact is in our opinion a strong candidate to explain, in thin sensors, the decrease of the current injection associated with the presence of NO_2 . If the presence of NO_2 leads to a shift of the Fermi level, it will accordingly affect the current injection as well. A model which include a Fermi level shift at the surface has been described by Boarino *et al.*⁸ In p^+ PSi, close the mid-gap energy, there is a high density of dangling bonds (D^0). In absence of gases, ionization of boron dopants can involve such defect states, which supply electrons ($B_3^0 + D^0 \rightarrow B_4^- + D^+$). Therefore, in p^+ PSi, ionization does not produce free holes, because of the trapping action of the defect states at the surface (D).⁸ The Fermi level remains between the energy levels of boron and defect states, as schematized in Fig. 3, (a). The presence of NO_2 bends the energy bands upward at the PSi surface, pulling the Fermi level below the boron energy, and restoring the original doping action of boron [Figs. 3(b) and 3(c)]. An interesting feature of this model is the energetically favorable location of holes at the outer surface of conductive paths. Thus, the effect of NO_2 is twofold: holes are de-trapped and pulled at the surface. There is a reduction of the effective conductive area [as in Fig. 3(b)] or more appropriately of the hole mobility, because of the larger scattering in proximity of the surface. If the hole density is very low (as in the thick sensor), in the absence of NO_2 there is hardly any conduction. The hole repopulation induced by NO_2 totally obscures any effect on mobility. On the contrary, if hole density is not negligible even in absence of NO_2 , a mobility reduction might be the only measurable effect of NO_2 . In the thin sensor, the hole density is higher than its equilibrium value because of diffusion from the junctions. The hole de-trapping by NO_2 has a negligible contribution to the overall hole density. Thus, we suppose that in thin sensors the only significant effect is the band bending, which reduces the effective mobility, increasing the resis-

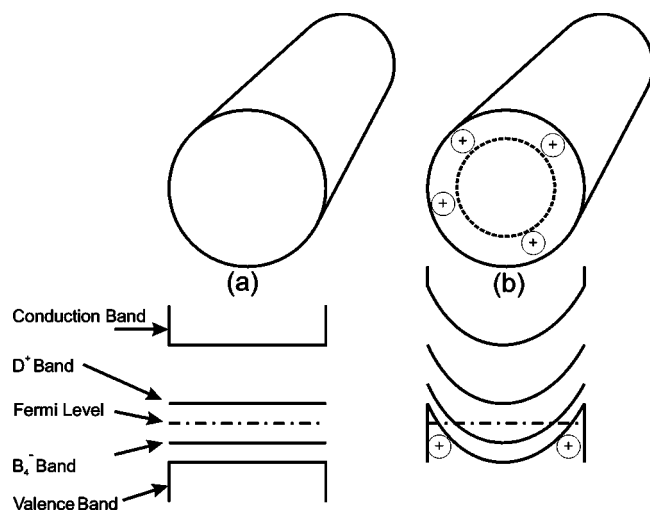


FIG. 3. Pictorial representations of a conductive path of *bulk* porous Si (thick sensor), in absence (a) and in presence (b) of NO_2 . The energy states of each case are qualitatively shown underneath. In the presence of NO_2 , the effective cross section of the conductive path is reduced by the band bending. In the thin sensor, free holes are present also in case (a), and their density is homogeneous across the wire section, since the bands are flat.

tance. If the bias is reversed, the situation is essentially the same, except that the roles of the two junctions are exchanged. The slight asymmetry of $I-V$ curves of thin sensors (Fig. 2) is probably due to this material asymmetry.

There can be some risk that gold creates some partial short cuts in this sensors, and that the decrease is originated by oxidation of gold under NO_2 exposure. However, it should be noticed that the dynamics of thin and thick sensors have strong similarity (Fig. 1). For this reason, we favor the explanation by the PSi/NO_2 interaction, which provides a common physical origin for the two opposite observations.

In conclusion, the effect of NO_2 on porous silicon is to increase the free hole density, simultaneously pulling them

toward the surface. The latter effect is an effective narrowing of the conductive cross-sections, which also implies a lowering of the effective hole mobility. In thin sensors, this latter effect dominates because the free hole density is high even in the absence of NO_2 . On the contrary, in thick sensors, the dominating effect is the increase in free hole density. As a consequence, the net effect of NO_2 in thick and thin porous silicon sensors is opposite in sign.

The authors acknowledge the support of INFN, progetto PAIS 2001 "SMOG," and of Provincia Autonoma di Trento.

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