APSFET: a new, porous silicon-based gas sensing device

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Abstract

In this paper, a new sensing device based on a FET structure having a PoSi layer as sensing material, namely adsorption porous silicon-based FET (APSFET), is proposed. The sensing mechanism is based on an gas-induced conduction channel in the crystalline silicon under the sensing layer, a new approach with respect to previously reported PoSi sensors. The fabrication process is based on a standard silicon process. In this work, the fabrication process along with an electrical characterization of the device in presence of different organic vapors (alcohols and acids) is presented and discussed.
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Keywords: Gas sensor; Porous silicon; Polar molecules; Alcohols; Organic acids

1. Introduction

Today's need to constantly monitor and control air pollution in the environment, in laboratories, hospitals or generic technical installations, pushes the development of highly sensitive gas detectors to prevent accidents caused by gas leakages. Such detectors should allow continuous monitoring of the concentration of particular gases in the environment.

Ideally, a gas sensor should have: (i) high sensitivity; (ii) high selectivity, i.e. negligible (or at least known and repeatable) response to other species; (iii) small size; and (iv) low cost. In the last years, a number of new sensing materials, apart from the standard thick film oxides, have been considered. The compatibility of such materials with integrated circuit (IC) fabrication processes would certainly be a remarkable advantage. As a matter of fact, the use of IC batch fabrication and the inclusion of extraction/conditioning electronics on the same chip would give a significant push in the direction of low cost/low size devices.

Because of its very large surface/volume ratio (hundreds of m^2/cm^3), high reactivity, and its potential compatibility with silicon-based electronics, porous silicon (PoSi) is one of the most promising materials for the fabrication of gas sensors. PoSi-based devices have been proposed as sensors for humidity [1,2], NO_x [3,4] and various organic polar substances [5,6]. The involved sensing mechanisms are generally associated with a change in the free carrier concentration in the porous layer due to adsorbed molecules, or changes in the dielectric constant due to gas condensation inside the pores; the sensed quantity is generally a conductance/current [7] or capacitance [2,8].

Optical methods, based on photoluminescence modulation [9], or interferometry [10,11] have been proposed as well, and very high sensitivities were demonstrated. Nonetheless, the use of optical detection implies a much more complex measurement system with respect to electrical methods, and this fact limits its usefulness in practical sensors.

Despite the large interest in PoSi based sensors, the compatibility of the fabrication process with the IC technologies has not been investigated in detail in the literature. Non-standard processes are generally used for PoSi sensors fabrication. An alternative to this approach is the modification of a standard IC technology with the addition of specific steps for PoSi fabrication. In this case, however, performing the anodization step (i.e. the PoSi formation) between standard process steps leads to severe compatibility problems for two main reasons: (i) the possible contamination from PoSi itself to other parts of the device/wafer and to the processing reactors (for instance when a contact metal layer is deposited directly on the PoSi after its formation), and (ii) PoSi degradation (mechanical, electrical, etc.) because of thermal and/or etching steps. Thus, in order to ensure the compatibility with the industrial processes the PoSi layer fabrication should be the last technology step [12].

Our device, an adsorption porous silicon-based FET (APSFET) is a gas sensor based on a standard bipolar + CMOS + DMOS (BCD) silicon technology. The porous layer is fabricated at the end of the process. In the APSFET, the change of the sensed quantity (a current) is

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caused by a change of free carrier concentration in the silicon channel directly below the porous sensing layer, with advantages in term of measurement and sensitivity. A similar mechanism is used for example in ISFETs [13], where protonation of the interface between the gate insulator and an aqueous solution results in a change of the channel conductivity, as well as in the ADFET [14], where the adsorption/desorption of polar molecules from a gaseous environment results again in a modulation of the conductivity of a FET device.

2. Device fabrication

The fabrication process of our device is based on an industrial BCD process and schematically consists of the following steps: (1) wet oxidation (about 90 nm) of a p type $\langle 1\,0\,0 \rangle$ wafer with a doping of 10^{15} cm^{-3}; (2) boron implantation through the oxide to create two interdigitated comb-like patterns, 1.4 μm deep, with an higher p-doping (pBody): grid lines are 4 μm wide, several hundreds micrometers long, and spaced 30 μm apart; (3) arsenic implantation to define an n$^+$ contact 0.23 μm deep on the pBody lines; (4) polysilicon deposition (450 nm) and polysilicon n$^+$ implantation; (5) polysilicon patterning to define the front contact (constituted by a poly/SiO$_2$ structure) and the lines to the sensing area; (6) deposition of an LPCVD Si$_3$N$_4$ layer with a thickness of 90 nm; this film acts as a masking layer during the anodization process, as will be clear later; (7) deposition of an spinnable SiO$_2$ (TEOS) layer (500 nm), to be used as a mask for the Si$_3$N$_4$ etching; (8) definition of a window onto the SiO$_2$ to expose the active area; the device area is 1 mm^2 approximately; (9) wet Si$_3$N$_4$ etching by means of an H$_3$PO$_4$ solution and (10) wet etch of the residual oxide. The final step was the selective anodization of the structure through the Si$_3$N$_4$ window. As the LPCVD nitride is etched at a very slow rate by the anodization solution, it can be used to define PoSi areas of arbitrary shape. The composition of the anodization solution was 1:1(v/v) HF (48%):C$_2$H$_5$OH (99.9%). After the anodization the samples were rinsed in ethanol and pentane and slowly dried in nitrogen ambient.

The anodization process, performed in the dark, acts only on p-doped silicon, whereas the n$^+$ poly/n$^+$ silicon are not affected [12]. In this way a p PoSi layer is formed and the n$^+$ poly/n$^+$ silicon contact is left unchanged, so that the formation of an electrical contact on PoSi after its formation is unnecessary.

It is important to note that, depending on the values of the anodization parameters (time and current density) two
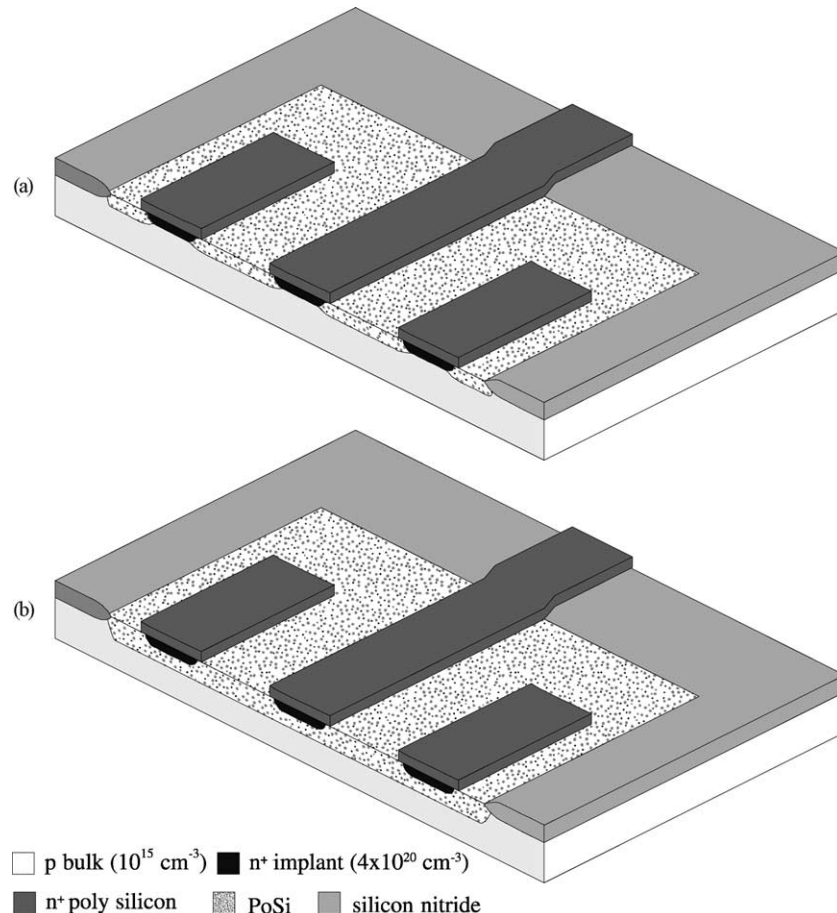

Fig. 1. Schematic view of the APSFET. In (a), a non-continuous device is shown, while (b) is a continuous one. For clarity, only three strips are shown.

different structures can be produced. For low currents/times, the PoSi layer is not continuous (i.e. connected) under the n^+ implant, while for higher currents/times the anodization takes place under the n^+ implant as well, and a continuous buried layer can be obtained [12]. The resulting structures are sketched in Fig. 1a and 1b, respectively. In the latter case, the n^+ strips are physically connected with PoSi only, and not with the crystalline bulk. In the following, we will refer to these two classes of devices as "non-continuous" (Fig. 1a) and "continuous" (Fig. 1b).

3. Experimental and discussion

The concentration of organic vapors was controlled by mixing pure nitrogen, used as a carrier gas, with a saturated vapor of the chosen substance. A nitrogen gas stream is injected at the bottom of a liquid-filled vessel (the saturator) and bubbles through the liquid phase. At the same time, the liquid evaporates into the gas bubbles until the equilibrium saturated vapor pressure, P_v, is reached. For a single compound this vapor pressure is a function of the temperature only and can be obtained through the Antoine equation. The mole fraction at the outlet of the saturator y_v' is given by:

$$y_v' = \frac{P_v}{P_{tot}} \tag{1}$$

where P_v is the vapor partial pressure and P_{tot} the total pressure.

In order to reach lower concentrations the saturation principle has been combined with the dilution technique. A known nitrogen flux, F_{car}, is fed through the saturator and is subsequently mixed with a larger diluting flux, F_{dil}.

After the secondary dilution, the mole fraction of the proportioning component y_v'' is:

$$y_v'' = \frac{\lfloor [y_v'/(y_v')] \rfloor}{1 + (F_{dil}/F_{car})}. \tag{2}$$

By varying the flux ratio, vapor concentrations as low as 100 ppm can be obtained. The temperature was controlled by placing the sample into a testing chamber equipped with a 0.1 °C resolution temperature controller. The chamber volume was about 200 cm^3.

Electrical measurements were carried out with an HP4145B parameter analyzer. All the currents were measured by biasing one of the two comb-shaped electrodes with respect to the other one, and by electrically connecting the latter with the back electrode (i.e. with the p-doped bulk). All the electrical measurements were carried out at atmospheric pressure and at a temperature of 30 °C.

Fig. 2 shows a typical current–voltage characteristics of a device for several isopropanol concentrations. The I–V curves resemble the output characteristics of a FET, with a linear region for low voltages and a saturation current at higher voltages. This type of characteristics was only observed in non-continuous samples, whose structure closely resembles a FET. On the contrary, in continuous samples typical conduction currents were about three orders of magnitude lower than in non-continuos devices. Also, the curve shape no longer resembled the output characteristics of a FET and was almost independent on the isopropanol vapors, up to concentrations of 20,000 ppm.

In Fig. 3 the transient response of the sensor c28 (anodized at 25 mA/cm^2 for 30 s), exposed to different isopropanol vapors concentration is reported. The graph clearly shows that the sample current is restored to its initial value after the
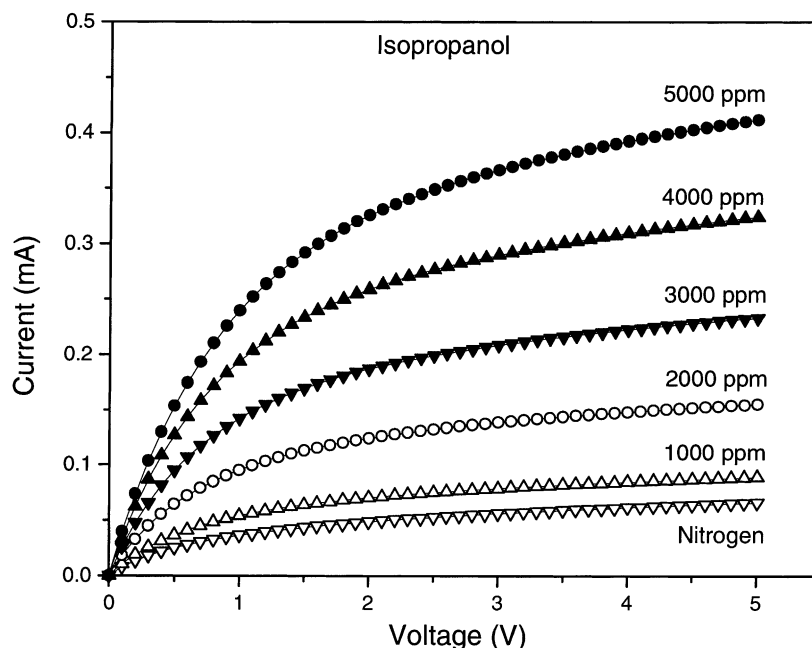

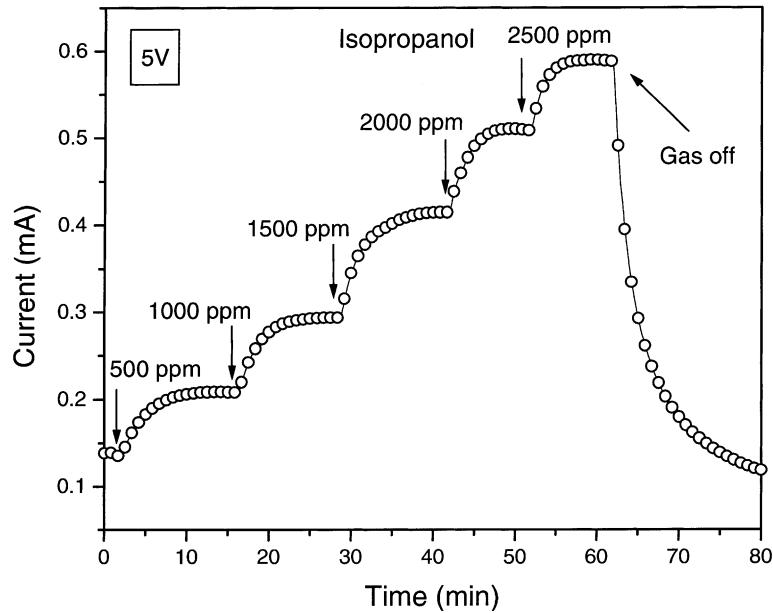Fig. 2. Current–voltage characteristics of an APSFET in presence of several isopropanol concentrations.

Fig. 3. Transient response of sample c28 for increasing isopropanol concentrations.

measurement cycle, i.e. the final current value (in absence of isopropanol) is very close to the initial value. The response time of the sensor cannot be easily extracted from these curves because of the large volume of the testing chamber.

In Fig. 4 the response of two devices to different isopropanol concentrations, at a constant 5 V bias, is reported. Sample c28 (circles) was anodized at 25 mA/cm^2 for 30 s, while sample c30 (triangles) was anodized at the same current density for 10 s only. Both the samples are non-continuous, but with different PoSi thickness (about 0.5 μm for c28, 0.15 μm for c30). The current for the sample c30

is consistently lower than for the other one. Moreover, a threshold value in the concentration exists for the former before the current starts to grow linearly. As shown in Fig. 5, once the thinner device is turned on (concentration above 2000 ppm), the sensor current linearly depends on the concentration up to 10,000 ppm.

In Fig. 6 the effect on the sensor current of C1–C4 alcohols at constant voltage bias (5 V) is reported. For every species the sensor response linearly depends on the concentration of the species in the environment. Moreover, the sensitivity of the sensor increases with the number of carbon
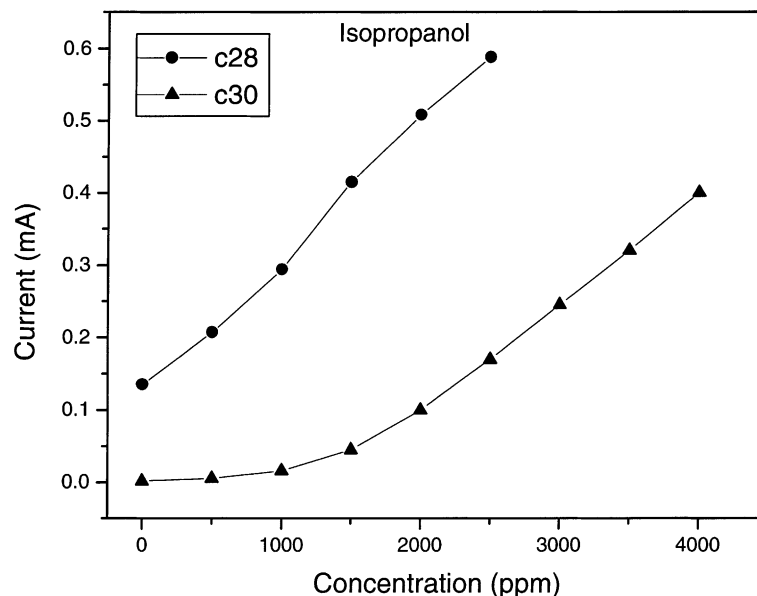

Fig. 4. Response of samples c28 (circles, thicker PoSi layer) and c30 (triangles, thinner PoSi layer) to different isopropanol concentrations.
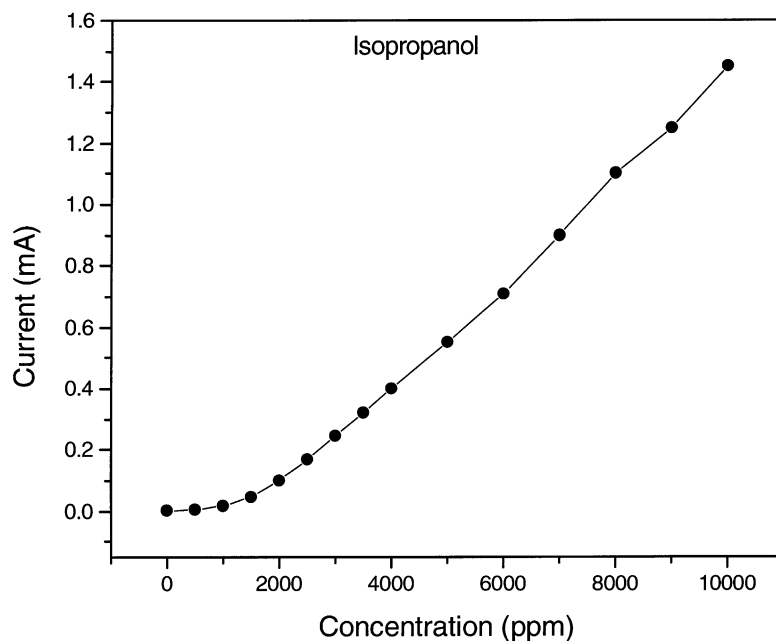
Fig. 5. Full-range (0–10,000 ppm) response to isopropanol for sample c30.

atoms in the molecule or the molecular weight of the molecule.

Interestingly, an opposite effect on the current was observed for organic acids [15] (we tested formic, acetic, propanoic and butanoic acid) with respect to alcohols. As an example, we give in Fig. 7 the *I–V* characteristics of a sensor after acetic acid exposure: a *reduction* of the conduction current is clearly observed.

There are several approaches to explain the variation of the current with the adsorbed gas. One of the most frequently

reported is associated with changes in the PoSi film capacitance and/or conductivity due to vapor condensation in the pores. The formation of a condensed phase in the pores changes the average permittivity (which can be capacitively sensed) and could also introduces a parallel ionic conductivity (as could be the case of ammonia [8]). However, conductivity variations well below the condensation conditions have been reported for methanol [16]. In our devices, the fact that the conductivity actually *lowers* for a class of substances (organic acids), while a parallel ionic conduction
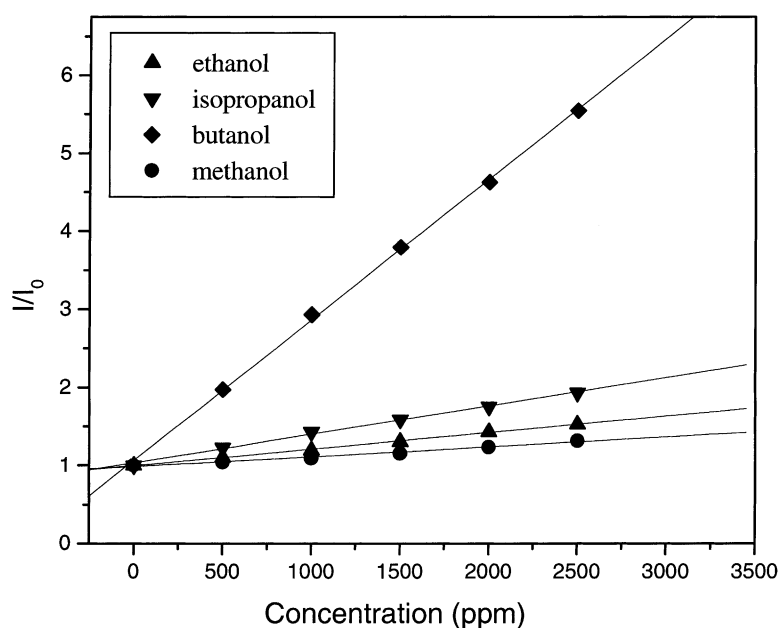

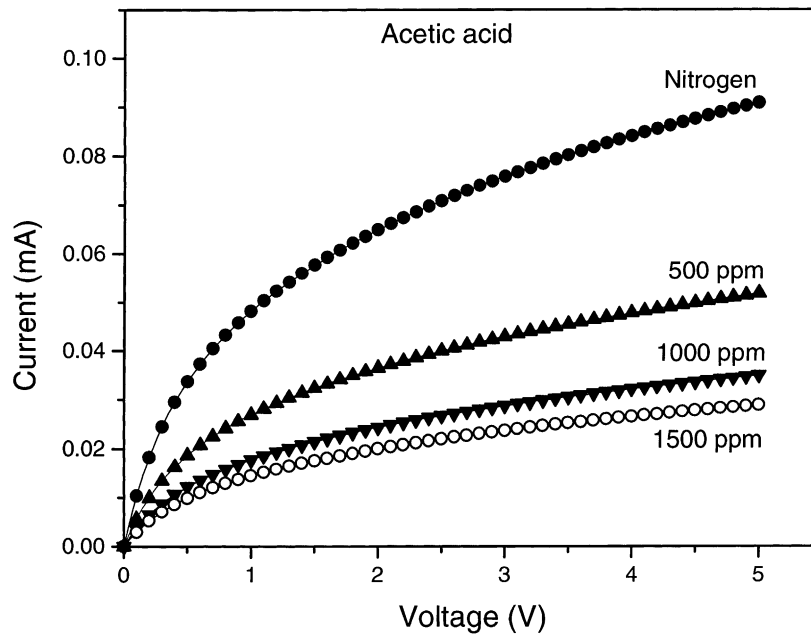Fig. 6. Response of an APSFET to the C1–C4 series of alcohols.

Fig. 7. Current–voltage characteristics of an APSFET in presence of several acetic acid concentrations.

mechanism should always raise the current, excludes that, at least for acids, this mechanism is responsible for the observed current changes.

Stievenard and Deresmes [17] proposed a model where adsorbed gas molecules at the PoSi surface change the width of a depleted region inside the silicon nanocrystals, thus modifying the overall conductance of the PoSi layer. It must be pointed out that, depending on the concentration of defects at the nanocrystals interface and the doping of the original bulk material, the nanocrystals could well be completely depleted, or even inverted (i.e. actually populated by electrons) even in absence of any adsorption. A low doping acts both in the sense of reducing the initial hole population in the nanocrystals and reducing the average size of nanocrystals. It is well established that nanoporous silicon is obtained starting from p type low doped material (see, for example, [18]). While this model could explain the behavior of continuous devices, where the observed slight increase in current could be interpreted as an increased concentration of carriers in the porous layer, the FET-like characteristics of non-continuous devices and their higher sensitivity (i.e. the higher conductance change for the same vapor concentration) with respect to the continuous ones cannot be easily modeled.

On the other hand, the structure of non-continuous devices suggests that a significant part of the conduction current flows through the crystalline material immediately below the PoSi layer. The current in non-porous (i.e. not yet anodized) devices is in the nA range—as expected for a reverse saturation current of a n^+–p junction—and the same is true for continuous devices (as stated earlier). On the contrary, a much higher current is observed in non-continuous devices.

This behavior is well explained by the presence of an inverted channel of mobile electrons in the crystalline p-doped layer under the PoSi layer and between adjacent n^+ contacts. If the adsorption of a molecule results in a change in net charge in the PoSi layer, a mobile charge sheet can be easily formed (or removed, depending on the sign of the PoSi charge) in the underlying crystalline silicon. A change in the number of adsorbed molecules per unit area results then in a modulation of the channel charge density and, in turn, in a change of the channel conductivity, with the same mechanism of a MOS transistor. It is known that an inverted channel can be induced in a MOS structure as a consequence of ions enclosed in the gate oxide or interface defect states: values as low as 10^{11} charged defects/cm^2 are sufficient to invert a substrate with doping $N_A = 10^{15}$ cm^{-3}. An enormous number of sites per unit area is available for adsorption in the PoSi, so that the channel charge density is expected to be extremely sensitive to the vapor concentration in the ambient.

An even stronger evidence of the formation of an electron channel at the PoSi-crystalline silicon interface is given in Fig. 4, where the current dependence on isopropanol concentration for two different, non-continuous devices at the same voltage bias is given. The only difference between the samples is the thickness of the porous layer. When the two samples are exposed to pure nitrogen, c28 (the one with thicker PoSi) already conduces more than 100 μA, while the current in c30 (the thinner one) is still negligible. Above a threshold isopropanol concentration (about 2000 ppm) both currents linearly depend on the concentration. This behavior is easily explained if we postulate that a non-negligible fixed charge is present in the PoSi matrix, which is known to have a large number of defects (among them dangling bonds) that

could act as charge traps. The density of defects per unit area is proportional to the PoSi layer thickness. Thus, the initial fixed charge in the thicker sample can be sufficient to induce a conduction electron channel even in absence of adsorption, while the thinner sample begins to conduce only when the charge contribution of the adsorbed isopropanol reaches a value that forces the underlying silicon substrate into strong inversion.

The adsorption mechanism and its influence on the carrier concentration is still not clear. The trend we observed for acids is coherent with the one reported in [14], where it is attributed to the behavior of different substances as Lewis acids or bases, that act as acceptors or donors for the underlying substrate if the gate oxide is sufficiently thin (less than about 5 nm). In our model, this charge plays the role of the gate charge in a MOS transistor. A role of the dipole field of the adsorbed molecules in the stabilization of free carriers at the nanocrystal interface was also suggested [16]. As a matter of fact, we observed no response to pentane, which is non-polar. Nonetheless, the dipole moment cannot fully explain the strong difference in current sensitivity that we detected for different alcohols, which show almost the same dipole moment (around 1.8 D). A more complex (yet unknown) interaction (chemical or physical) of these species with the PoSi network has to be supposed. Also, a dipole-based model cannot explain the reduction of conduction current in presence of organic acids.

4. Conclusions

An alcohol/acid-selective, integrated porous silicon sensor based on a FET-like structure (or APSFET) was presented. Its fabrication technology is compatible with standard IC technology—as a matter of fact, apart from anodization, that comes as the last step, it was fabricated using a standard technology. Because of the high area/volume ratio of PoSi, high sensitivity and high output currents are achievable. The presented data strongly suggest that the working principle of the APSFET is based on a modulation of the mobile charge at the porous silicon-crystalline silicon interface, and that this modulation is induced by the adsorption of molecules of the sensed species inside the porous silicon matrix.

Acknowledgements

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