Gas sensors based on silicon devices with a porous layer

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In this work two silicon devices, that is a FET and a p crystalline silicon resistor having porous silicon as adsorbing layer are presented as gas sensors. Owing to they are easily integrable with silicon electronics, these devices could represent an improvement of the functionality of silicon for sensor applications. Unlike other porous silicon-based sensors, in this case the sensing variable is a current flowing in the crystalline silicon, so that the porous silicon film has only the function of adsorbing layer and its properties, electrical or optical, are not directly involved in the measurement. The fabrication processes and an electrical characterization in presence of isopropanol vapors are presented and discussed for both devices.

1 Introduction

Porous silicon (PS), owing to its huge surface/volume ratio, is able to adsorb a great amount of gas molecules. This unique PS feature allows the design of solid-state silicon sensors using PS as sensing layer. Several approaches have been proposed in which the measured quantity is a conductance/current [1] or a capacitance [2] variation (electrical methods) as well as a photoluminescence spectrum change [3–5] (optical methods) of the PS layer. It was demonstrated in a previous paper [6] that PS production is compatible with integrated circuits fabrication processes, so that it could be interesting to design gas sensors based on the well known characteristics of integrated silicon devices, in which the PS layer acts only as a gas sensing film and its electrical, or in some cases optical, characteristics are not involved. On this subject it must be noted that the transport properties of PS are not yet well known and they easily change as a function of the etching parameters, such as current density, solution composition, intensity of illumination and temperature, unless they are carefully controlled.

The working principle of the sensors proposed in this paper is based on the fact that any change induced by the adsorbed gases in the PS film influences the space charge layer at the interface PS/crystalline silicon, in the same way, for example, of charges in the gate oxide of a MOSFET. Besides, owing to the electrical characteristics of a conventional device can be easily simulated, once its geometrical structure and doping profiles are known, the proposed devices could be useful to investigate the phenomena occurring in the PS film, at least at the interface with the silicon bulk.

The devices designed and fabricated are: i) a FET provided with a PS layer between drain and source terminals (APSFET: Adsorption Porous Silicon Field Effect Transistor) and ii) a p silicon resistor with a PS layer on its top as sensing layer. The devices differ in the mechanisms of conduction: in the APSFET the current flows in the inversion layer of the FET (electrons); in the resistor the transport is due to the majority carriers (holes).

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2 Fabrication of the devices

The APSFET fabrication process was extensively described in a previous paper [7] and it will be only schematically reported here. An industrial standard BCD (Bipolar + CMOS + DMOS) process was employed to produce the FET structure which was subsequently post-processed to form the PS layer. The basic steps were: 1) wet oxidation of a \textit{p} type \textless 100\textgreater wafer \((N_A = 10^{15} \, \text{cm}^{-3})\); 2) boron implantation through the oxide to form two interdigitated comb-like patterns, 1.4 \(\mu\)m deep, with an higher \textit{p} doping \((p_{Body})\); 3) arsenic implantation to define an \textit{n'} contact 0.23 \(\mu\)m deep on the \textit{pBody} lines; 4) polysilicon deposition (450 nm) and polysilicon \textit{n'} implantation; 5) polysilicon patterning to define the front contact (constituted of a poly/SiO\(_2\) structure) with the lines on 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; 7) deposition of an SiO\(_2\) (TEOS) layer (500 nm), to be used as a mask for the Si\(_3\)N\(_4\) etching; 8) opening of a window onto the SiO\(_2\) to expose the active area; 9) wet Si\(_3\)N\(_4\) etching; and 10) etch of the residual oxide. The final step was the selective anodization of the structure through the Si\(_3\)N\(_4\) window. As the nitride is etched at a very slow rate by the anodization solution, it can be used to define PS areas of arbitrary shape. The anodization process, performed in the dark, acts only on \textit{p} silicon, whereas the \textit{n'} poly/\textit{n'} silicon are not affected [6]. In this way a \textit{p} PS layer is formed and the \textit{n'} poly/\textit{n'} silicon contact is left unchanged. The top view and section of the APSFET are sketched in Fig. 1 (left).

In Fig. 1 (right) the top view and a section of the resistor are shown. The sections of both devices are made along the dotted lines SS'. The resistor is integrated on a \textit{p} layer 2.3 \(\mu\)m deep, obtained by boron implantation in a \textit{n} type wafer \(<100\textgreater\) orientation, resistivity \(1.5 - 4 \, \Omega \cdot \text{cm}\) through an oxide film (about 55 nm). The surface doping resulted to be \(10^{17} \, \text{cm}^{-3}\). After the complete etching of the oxide, Al was deposited on the \textit{p} side and annealed in N\(_2\) flow at 400 °C. A first mask was used to define two interdigi-

![Fig. 1 Schematic top view (top) and cross-section (bottom) of fabricated gas sensing devices: the APSFET in the left; the resistor in the right.](image-url)
tated Al resistor contacts. Then aluminum contacts were protected by using a photoresist layer (second mask) hardened at 130 °C for 30 min to withstand the electrochemical etching step in HF for the time required to the PS formation. An Al layer was deposited on the back of the sample by thermal evaporation. Finally, the porous layer was selectively performed through the photoresist windows. This step is critical because: 1) the hardbaked photoresist layer can not withstand the anodization phase for times greater than few minutes (H₂ evolution from the sample surface breaks off the resist layer); 2) anodization have to be performed with a suitable choice of the etching parameters in order to obtain the proper thickness of the bulk resistor,  \( t \) in Fig. 1 (right). The device is provided with a third electrode, that is the  \( n \) silicon bulk, which can be used to modulate the resistance value of the resistor.

The composition of the anodization solution was 1:1(vol.) HF (48%):C₂H₅OH (99.9%) for both devices. The anodization parameters were: 25 mA/cm² and 30 seconds in the APSFET case; 50 mA/cm² and 60 seconds for the resistor. In the latter, a constant illumination (50 W halogen lamp at a distance of about ten cm) was used for the whole anodization time. After the anodization the samples were rinsed in ethanol and pentane and slowly dried in nitrogen ambient. Both the sensors were finally mounted on TO8 metal packages with a non-welded cap for electrical measurements.

3 Measurements and discussion

The measurement setup consists of: 1) a leakage proof test chamber with a volume of about 100 cm³ whose temperature can be monitored and controlled; 2) a system for the adduction and mixing of gases, equipped with mass flow meters. Organic vapors to be monitored were obtained by feeding a pure nitrogen flow  \( F_{\text{car}} \), used as a carrier gas, through the liquid phase of the chosen substance (saturated flow). The proper value of vapor concentration was obtained by diluting the saturated flow: the saturated flow is mixed with a larger diluting flow,  \( F_{\text{dil}} \), so that by varying the carrier-dilution flow ratio it is possible to obtain vapor concentration as low as 100 ppm. The vapor tested in this work is isopropanol (ISO). All electrical measurements were carried out at atmospheric pressure and room temperature.

As far as the APSFET is concerned, the I-V characteristics were recorded with the source terminal connected to the p substrate and the PS layer acting as a floating gate (see Fig. 1(left)). Some typical charac-

![Fig. 2](image)

**Fig. 2** Typical current-voltage characteristics (left) and transient response (right) of the APSFET in presence of nitrogen and isopropanol vapors.
involve an increase of $Q_s$, the positive charge per unit area in the PS layer. Transient times were tens of minutes both for the rise and the fall times as can be seen in Fig. 2 (right). The sensor current completely recovered its initial value when ISO was removed by a nitrogen stream.

The I-V characteristics of the resistor were recorded by biasing one of comb-shaped aluminum electrodes (HIGH) with respect to the other one (LOW in the Fig. 1 (right)). Moreover, in order to reduce current leakage toward the bulk (n silicon) and ensure that all the current flowed through the p crystalline resistor, the bulk was connected to a higher positive voltage than the HIGH terminal (see Fig. 1(right)). A typical I-V curve of the sensor in N$_2$ atmosphere and in the presence of 15,000 ppm of ISO vapors is shown in Fig. 3(left), for two different bulk voltage polarization (1 and 5 V). It is evident that exposure to ISO vapors reduces the resistance value $R$ of the p crystalline resistor but the linear behavior is maintained. In this case the adsorption/desorption transients can be estimated of some tens of seconds and some hundreds of seconds, respectively (Fig. 3 (right)). Both the adsorption and desorption time are quite different from the APSFET case. The reason of these different behaviors is still unclear and could be related to the different doping of p silicon in the two devices from which the PS layer is obtained. As in the case of the APSFET, the current sensor is completely recovered when ISO vapors are removed from the test chamber. By changing the bulk voltage, the value of $R$ in N$_2$ increases (the pn depletion zone widens) and also $\Delta R$ increases (see Fig. 3 (left)): for the same space charge effect at the PS/p silicon interface the percentage variation of the resistor cross-section is greater. The presence of this third electrode allows to tune the sensitivity of the device.

By comparing the results obtained for both devices some facts could be inferred. It seems that in the case of the APSFET the gas adsorption raises the localized positive charge in the PS layer thus inducing a conducting inversion layer in the crystalline silicon under the PS itself [7]. In the case of the resistor instead, the gas adsorption causes a reduction of the $R$ value. There are in this case two possibilities: 1) p crystalline silicon at PS/p silicon interface is depleted. In this case, a decrease of $R$ value means a reduction of the extension of this depletion zone which, being formed by negative acceptors, reduces its extension if the positive charge $Q_s$ on the PS diminishes; 2) an accumulation layer of free holes exists in the p crystalline silicon at PS/p silicon interface. Even in this case a decrease of $R$ value could be explained with an increase of the free charge density in this layer; this happens only if the negative charge $Q_s$ on the

![I-V curve](image1)

**Fig. 3** Typical current-voltage characteristics (left) and transient response (right) of the resistor in presence of nitrogen and isopropanol vapors.
PS increases. It is evident that the results obtained from two different kinds of sensor devices are not in agreement. This circumstance could be due to the different doping of the p silicon from which the PS layer was formed and thus to completely different surface chemical and physical characteristics of PS itself. Another possibility is that the space charge interpretation could be not accurate and other models should be investigated. Nevertheless, it must be noted that in these devices the current variations recorded in both cases can not be ascribed to an additional current flow in the PS layer induced by the adsorbed species. In order to rule out this hypothesis, a suitable experiment was performed, as shown in Fig. 4. The anodization step was prolonged until the PS layer: i) excluded any crystalline path between the contacts of the APSFET and ii) extended to the n silicon in the resistor case. In fully-porous devices (Fig. 4) the electrical current must flow in the PS layer. By the way, in fully-porous devices the current was three order of magnitude lower than in non-fully-porous ones (Fig. 1) and did not show any appreciable increase as a consequence of adsorption of any quantity of ISO vapors.

4 Conclusions

In this paper two PS-based sensors have been fabricated and characterized. They differ from the traditional ones because the variable, in both cases a current, belongs to bulk silicon thus avoiding any direct interaction with the adsorbing PS layer. It was proved that the APSFET is fully compatible with an industrial process and that the resistor requires a very simple fabrication process, for which only two masks are necessary, so that both the devices could be easily integrated with the control electronics. The sensing mechanism is probably due to a space charge modulation effect induced by the adsorbed species in the PS layer, whose structure determines in a critical way the sensor behavior.

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References