

Fabrication and characterisation of a new sensing device based on hydrocarbon groups (CH_x) coated porous silicon

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Available online 21 February 2004

Abstract

In this work, we have fabricated a gas-sensing device based on hydrocarbon groups (CH_x)/porous silicon (PS) structure. The porous layer was prepared electrochemically from p-type silicon. The porous samples were coated with hydrocarbons groups (CH_x) deposited by plasma of methane under argon atmosphere.

We found that heterojunction fabricated from thin CH_x layer shows a good rectifying behaviour. This property, correlated with the porous silicon sensitivity to the gas environments, can be effectively used to realise heterojunction diodes whose current–voltage (I – V) characteristics are modified by the gas reactivity on the porous surface.

Sensitivity of those devices, response time and impedance response to different gas exposure (ethylene, ethane and propane) have been investigated.

FT-IR spectroscopy measurements in different gas environments show a reversible free-carrier detrapping in the IR region.

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Keywords: Porous silicon; Hydrocarbons groups; Gas-sensor; Ethylene; Ethane; Propane

1. Introduction

The interest in environment issues, particularity in pollution, has become in the last years a major key factor in the industrial development. Application of porous silicon (PS) for gas-sensing devices is quite recent. Generally, porous silicon sensing properties observed are changes of electrical capacitance and conductance in presence of gases and the quenching of photoluminescence [1–3]. The former has been found useful for humidity sensors [4]. A high sensitivity of the PS layer was also shown for organic vapours such as ethanol, methanol or acetone with high dipole moments [5,6]. However, the electrical response of the PS layer for these organic vapours can lead to a remarkable differences depending on the oxidation of the PS surface [7].

In this work, we have fabricated a gas-sensing device based on hydrocarbons (CH_x)/porous silicon structure. The porous layer was prepared electrochemically from p-type silicon in aqueous HF. The porous samples were coated with hydrocarbons groups deposited by plasma of methane. Sensitivity, response time and capacitance response of these devices to different gas exposure (ethane, ethylene and

propane) have been investigated. We found that heterojunction fabricated from thin CH_x layer shows a good rectifying behaviour. This property, correlated with the porous silicon sensitivity to the gas environments can be effectively used to realise a new sensing devices whose current–voltage (I – V) and capacitance–voltage (C – V) are modified by the gas reactivity on the porous surface. Finally, FT-IR spectroscopy measurements in different gas environments show a reversible free-carrier detrapping in the IR region.

2. Experimental

Porous silicon was obtained by electrochemical etching of p-type silicon wafer (1–10 Ωcm resistivity). The etching solution was prepared by adding 50 vol.% of ethanol to 50 vol.% of HF aqueous solution (49 wt.%). Current density and etching time were varied to obtain porosity ranging from 40 to 85% and thickness of PS layer 1–15 μm , respectively. The CH_x films were deposited by plasma of methane created in a RF (13.5 MHz) synchronised triode reactor under argon atmosphere on a PS surface. More details on the deposition procedure are described in [8,9].

The sample was placed in a small stainless steel vacuum chamber kept at 20 °C, connected by a valve to gas bottles. The gaseous species comes from certified bottles.

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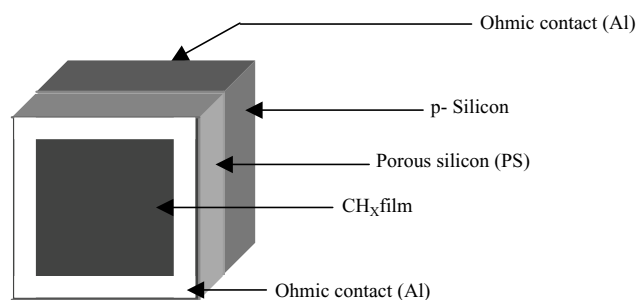


Fig. 1. A schematic diagram of the sensor.

Voltamperometric and capacitance technique were employed for sensor dc electrical characterisation in a controlled gas environment.

The IR spectra were collected by a thermo Nicolet Nexus Fourier Transform infrared Spectrometer equipped with a DTGM KBr detector. All FT-IR spectra were recorded in transmission mode in the IR region $400\text{--}4000\text{ cm}^{-1}$ at 4 cm^{-1} resolution.

Sensor prototype structure of $4\text{ mm} \times 4\text{ mm}$ cells was realised, Fig. 1. Metallic contact was achieved by the deposition of 99.99% pure Al on the backside of the PS sample. The Al contact on the CH_x layer was in the form of a frame of about $250\text{ }\mu\text{m}$ wide sides. The rest of the PS surface was CH_x coated.

3. Results and discussion

3.1. Dc electrical characterisation

In order to evaluate the response and sensitivity of heterostructure devices to different gas environments, the current–voltage characteristics were studied. The current

response was analysed for -2 to $+5\text{ V}$ bias voltage against ethylene, ethane and propane gases. Fig. 2 shows the (I – V) curves of $\text{CH}_x/\text{PS}/\text{Si}$ structure under vacuum and in environment saturated with ethylene gas. Vacuum is used in order to measure gas sensitivities without air contamination (CO_2 , O_2 , . . . , etc) and to understand the reaction mechanism between gases and $\text{CH}_x/\text{porous silicon}$ structure. A rectifying behaviour can be seen for the two cases. However, the ethylene gas introduces, more rectifying characteristics in the system.

The exposure to gases didn't changes the shape of (I – V) dependence but only changes the current magnitude at the fixed voltage.

At the maximum applied voltage of $+5\text{ V}$, the variation of the current is about $11\text{ }\mu\text{A}$ when the gas is introduced into the chamber. Such results indicates that the sensitivity is enhanced effectively at high voltage. While (I – V) curves had quite a small slope below the applied voltage of $+1\text{ V}$. The gases tested cause a reversible change of (I – V) characteristics parameters.

Fig. 3 shows the dynamic response of the sensor towards two concentrations of ethylene. A large current variation is observed for all ethylene concentration tested. The current recovers rapidly and completely to the initial value. At 3.5 V applied voltage, the response and recovery times at 115 ppm are of about 3 and 7 min, respectively. The maximum sensitivity recorded at 115 ppm and 345 ppm are of 5 and $8.6\text{ }\mu\text{A}$, respectively.

The change of the current, ΔI as a function of polarisation for the gases studied is depicted in Fig. 4. A constant variation is observed at potentials higher than 4 V , for ethylene, ethane, and propane, respectively. Of the gases studied, at the same gases concentration of 575 ppm the greatest relative variation is obtained for ethylene ($\Delta I/I_o \sim 26.75\%$), the sensitivity to ethane ($\Delta I/I_o \sim 13.7\%$) is also large and the

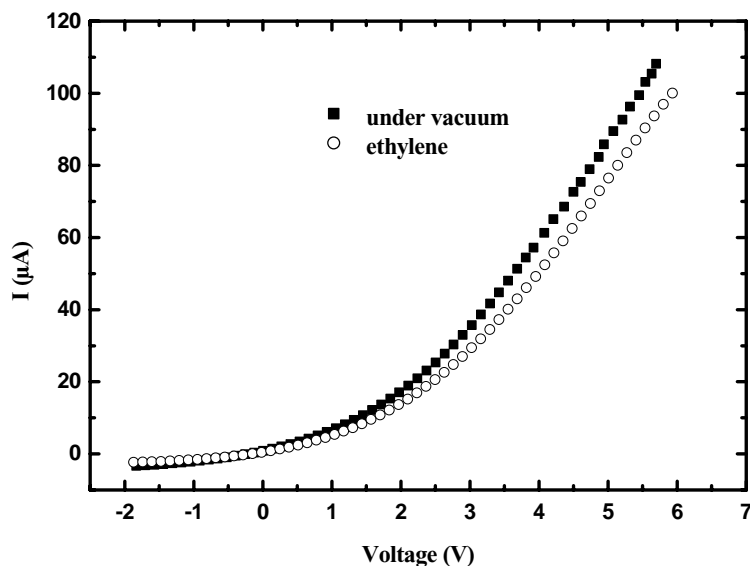


Fig. 2. (I – V) characteristics of a $\text{CH}_x/\text{PS}/\text{Si}$ structure, (a) under vacuum and partial pressure of ethylene (b).

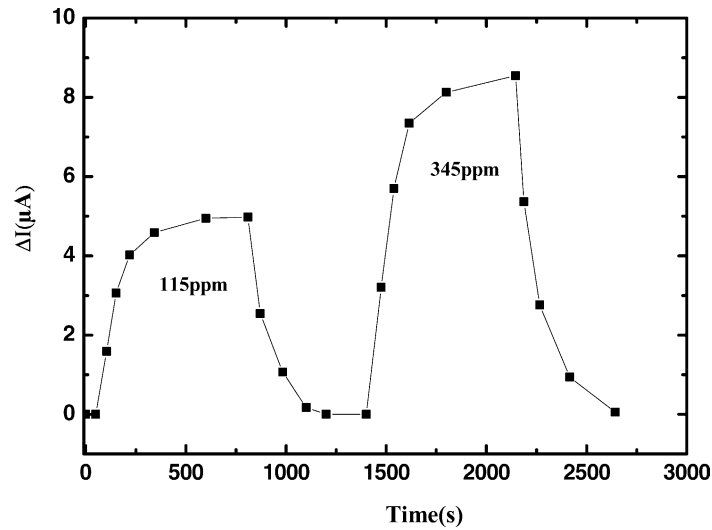


Fig. 3. Dynamic response of CH_x/PS/Si sensor to ethylene gas.

lowest response is obtained for propane ($\Delta I/I_0 \sim 9.4\%$). This behaviour can be explained by the steric hindrance of the gas molecules at the CH_x/PS surface.

Indeed as it can be shown from Fig. 4 the sensitivity decreases with the increase of the steric hindrance of the gas molecules in the order of ethylene < ethane < propane.

When the gas is removed, the phenomenon is reversible and we observe a non-exponential decrease of the current.

We have observed a variation of the current for the following gases ethylene, ethane and propane. However, using a gas-sensors based on PS/alumina structure, Boarino et al. [1] detected a low current variation for ethanol (1000 ppm), while no variations were recorded for ethylene (200 ppm) or CH₄ (15,000 ppm), gases with zero dipolar moment.

3.2. Capacitance measurements

Chemical sensors based on PS layers are generally used to examine the chemical concentrations in the liquid or gas phase by observing a variation of conductance or capacitance of these devices.

The characterisation of the device is undertaken by varying the frequency in the range 10 Hz–1 MHz. Fig. 5, which gives the variations of the capacitance versus bias at 5 KHz, shows that the samples behave as metal-insulator-semiconductor (MIS) structures. The introduction of the gas ethylene in the chamber induces a change in the capacitance–voltage values curve. The capacitance of the junction is determined by the displacement current through the ‘insulator’ layers. The change in electrical capacitance

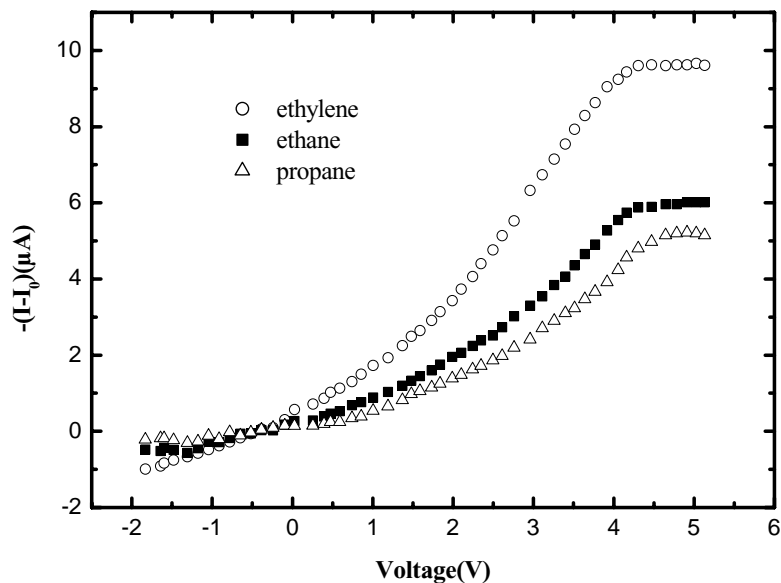


Fig. 4. Current variation (I) vs. voltage of the sensor for ethylene (a), ethane (b) and propane (c). Gases concentration 575 ppm.

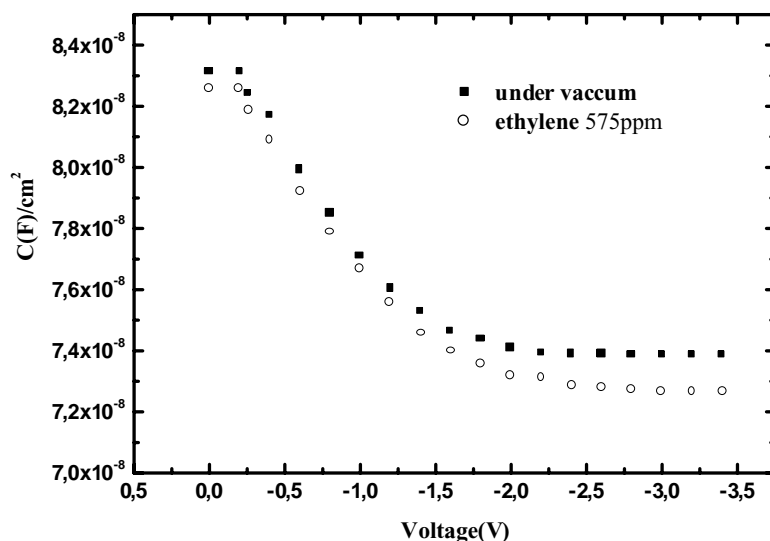


Fig. 5. Capacitance–voltage of a $\text{CH}_x/\text{PS}/\text{Si}$ sensor measured a 5 KHz, (a) under vacuum and partial pressure of ethylene (b).

can be explained in terms of dielectric constant variation or dielectric induced changes in carrier concentration due to molecular adsorption. However, more work and detailed measurements are needed to clarify this point.

3.3. FT-IR spectroscopy

FT-IR spectroscopy has been used extensively in the characterisation of the environment of hydrogen and NO_2 in porous silicon [10,11]. In order to evaluate the phenomena occurring at the surface of the $\text{CH}_x/\text{PS}/\text{Si}$ structure when it interacts with gases we have studied, FT-IR spectroscopy measurements have been performed. Fig. 6 shows IR absorption spectra of the same sensor sample exposed to different situations. Spectrum 1 correspond to sensor sample at room temperature. A strong broad band is observed

at about 2900 cm^{-1} due to C–H stretching vibrations mode, indicating the relatively high hydrogen content in the CH_x films. The absorptions at about 1450 and 1380 cm^{-1} correspond to in-phase and out-phase bending vibrations of the $\text{sp}^3\text{ CH}_3$ [11]. The weak absorption at 1155 cm^{-1} is due to the in plane C–H angle deformation. It was shown by Dischler et al. [12] that the area of C–H stretching bands was proportional to the total amount of bonded hydrogen.

The weak band centred around 1600 cm^{-1} must be ascribed to stretching vibrations of C=C double bonds [13]. One can observe the sharp band centred around 1710 cm^{-1} , which must be described to stretching vibrations of C=O double bonds. Finally, the absorption bands centred at about 2100 cm^{-1} are attributed to the vibrational modes of the SiH_x species.

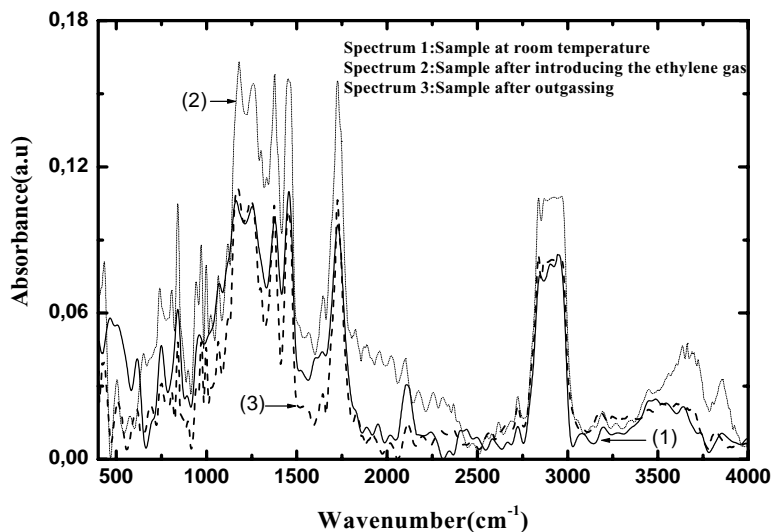


Fig. 6. FT-IR spectra (absorption) obtained after dosage of ethylene on CH_x/PS structure (spectrum 3). Spectrum 1 is related to sample outgassed under dynamic vacuum, spectrum 3 has been recorded after outgassing the sample, under dynamic vacuum.

Spectrum 2 has been obtained after introducing the ethylene gas in the sample chamber: (i) a featureless and intense absorption is formed, markedly evident at $\nu < 2800 \text{ cm}^{-1}$; (ii) the absorption bands related to the various CH_x and C=O modes are not influenced markedly; (iii) no new bands related to species in the absorbed state (i.e. absorbed at the PS surface) are formed. However, the absorption bands related to the various SiH_x modes are influenced markedly. The observed featureless absorption, characteristic of a loss of transparency of the sample can explain this behaviour. This phenomenon is observed in the case of semiconductor or non-stoichiometric oxides [1]. The loss of transparency in the mid-IR ($\nu < 3000 \text{ cm}^{-1}$) is assigned to the absorption due to free electrons in the conduction band and/or electronic transition [1,14].

Finally, spectrum 3 has been recorded after outgassing the sample at room temperature, under dynamic vacuum. It is evident that removing ethylene from the phase leads to the almost total restoration of initial condition.

We can comment that: (i) gas admission markedly modifies the spectral shape; (ii) removing ethylene, ethane or propane almost restores the initial transparency; (iii) admission of air on the outgassed samples completely restores the initial condition (spectrum 3).

The oscillations in this spectrum are due to the interference fringes related to the multiple reflections inside the transparent membrane. The mentioned effect is due to a loss of transparency of the sample to the IR beam and it is likely caused by free-carrier absorption.

The huge sensitivity of this material is explicable only in terms of electronic transfer from valence band to gaseous ethylene or by electronic localisation in chemical bonding.

FT-IR spectroscopy demonstrates a chemisorption phenomenon not yet fully understood. Both porous silicon and CH_x layer are responsible for strong band bending at silicon surface, causing depletion or even inversion phenomena, depending on the morphology (porosity) and impurity level of PS [15].

Several approaches have been invoked to explain the variation of the current. The most popular is associated with the condensation of the gas in the pores. However, this approach has been ruled out by Ben-Chorin et al. [16]. Stievenard and Deresmes [17] proposed that the conductivity is governed by the density of charges trapped on the interface state probably the effect of the gas is to passivate the active dangling bonds. Therefore, the mechanism of the current response can be explained by both the electrical transport properties in $\text{CH}_x/\text{PS}/\text{Si}$ diode structure and the charge transfer reaction that occurs during the adsorption at the PS surface.

4. Conclusion

We fabricated a new gas-sensing device based on $\text{CH}_x/\text{PS}/\text{Si}$ structure. It was found that heterojunction realised from CH_x thin layer showed a good rectifying be-

haviour. This property, correlated with the porous silicon sensitivity to the gas environments, has been used to fabricate heterojunction diodes whose current–voltage and capacitance–voltage were modified by the gas reactivity on the porous surface.

FT-IR measurements in ethylene, ethane or propane environment show a reversible free-carrier detrapping in the IR region of the spectra. However, more work in this fields will be carried out to obtain more information about the molecular dynamics at the surface of $\text{CH}_x/\text{porous silicon}$ structure in presence of gases.

Acknowledgements

This work was partially supported by Algerian Government PNR (02/UDTS/98). The authors gratefully acknowledge Ms. Karima Beldjilali.

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Biographies

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