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CO_2 and H_2 detection with a CH_x/porous silicon-based sensor

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Abstract

There has been great interest in the last years in gas sensors based on porous silicon (PS). Recently, a gas sensing device based on a hydrocarbon CH_x/porous silicon structure has been fabricated. The porous samples were coated with hydrocarbon groups deposited in a methane argon plasma. We have experimentally demonstrated that the structure can be used for detecting a low concentration of ethylene, ethane and propane gases [Gabouze N, Belhousse S, Cheraga H. Phy State Solidi (C), in press].

In this paper, the CH_x/PS/Si structure has been used as a sensing material to detect CO_2 and H_2 gases. The sensitivity of the devices, response time and impedance response to different gas exposures (CO_2, H_2) have been investigated.

The results show that current–voltage and impedance–voltage characteristics are modified by the gas reactivity on the PS/CH_x surface and the sensor shows a rapid and reversible response to low concentrations of the gases studied at room temperature.

Keywords: Porous silicon; Gas sensor; Hydrogen; Carbon dioxide

1. Introduction

Controlling and monitoring of CO_2 and H_2 partial pressures are of great importance in environmental and industrial fields. Hence, it has become necessary to develop cheap and stable CO_2 and H_2 gas sensors with high sensitivity and selectivity. Interesting results have been obtained in the last years in the fabrication of CO_2 and H_2 gas sensors [1–6]. However, such sensors although able to detect hydrocarbon compounds, are not able to distinguish among them. In addition, the solid electrolyte used in the gas sensors would easily vaporise at high temperatures.

Recently, we have developed a sensor based on porous silicon (PS). This is a CH_x/PS/Si sensor that is simple and offers the possibility of identifying organic gaseous such as ethylene, ethane and propane [7].

In this work, we report on the ability of the sensor to detect CO_2 and H_2 gases. It was shown that the gas sensor can operate at voltages in the range 10–100 mV demonstrating a sensitivity range at least between 100 and 1700 ppm. In addition, the results show that the conduction mode varies depending on the nature of the gas.

2. Experimental

Porous silicon layers were prepared from p-type Si, (1 0 0) oriented boron-doped (1–10 Ω cm resistivity) by electrochemical etching in a solution of a HF (49 wt%) ethanol solution of 1:1 (by vol) at current density of 100–500 A/m^2. The etching time was adjusted in order to obtain a porosity ranging from 40% to 85%. The PS thickness was varied from 1×10^{-6} to 10×10^{-6} m.

The CH_x films on the porous layer were deposited by using a methane/argon mixture in a RF (13.5 MHz) synchronized triode reactor [8]. A gas sensor structure of $(4 \times 4) \times 10^{-6}\,m^2$ cells was formed. More details on the structure fabrication have been described elsewhere [7,9].

The sensor was placed in a stainless-steel vacuum chamber ($1.43 \times 10^{-3}\,m^3$ vol) kept at room temperature and connected by a valve gas bottles containing the gases to be tested.

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Capacitance and impedance measurements were performed using an EG&G model 410 *C–V* plotter impedance meter.

3. Results and discussion

3.1. Current–voltage characteristics

The current–voltage (*I–V*) characteristics of the CH_x/PS/Si structure, was analysed for a −2 V to +5 V bias voltage change against CO_2 and H_2 gases. Figs. 1(a) and (b) show the *I–V* curves of the sensor under vacuum and in CO_2 and H_2 gases at 500 ppm pressure, respectively. For both Figs. 1(a) and (b) we observed, under +2 V forward polarisation a variation of the current up to 10 mA, whereas it is only 1 mA under −2 V reverse polarisation. For that reason, all the measurements were done under forward polarisation. One can observe that for positive bias voltage the variation $\Delta I = I - I_0$ is positive for CO_2 and negative for the case of H_2 gas indicating the passivating effect of hydrogen on the CH_x/PS/p-Si structure, where I_0 and I correspond to currents acquired before and after contact with gas, respectively. The absorption of CO_2 modifies the concentration of holes at the CH_x/PS surface. The donor states at the surface capture holes and increase the conductivity [10].

In addition, it is shown that for applied potential higher than +4.5 V, ΔI–*V* follows the same variation as the *I–V* characteristic while, for potential values above 4.5 V, ΔI is constant for both gases (CO_2 and H_2), indicating a behaviour similar to that observed previously for ethylene and ethane gases [7,9]. Moreover, the change in the gas concentration induces a variation of ΔI and becomes constant at a pressure above 1400 ppm. Fig. 2 shows the variation of current (ΔI) with gas pressure for the two gases studied, at 5 V applied bias. It shows that sensitivities increase with gas pressure.

Figs. 3(a) and (b) show the absolute sensitivity ($|\Delta I|/I_0$) of the sensor as a function of polarisation, for gases CO_2 and H_2, respectively. It shows that for both gases the highest sensitivities are observed for low applied bias voltage.

A maximum sensitivity value is found at about 50 mV bias voltage for CO_2, while for hydrogen the maximum sensitivity is found at 30 mV. These results indicate that the sensor can operate at low bias voltage in the 10–50 mV range with a high sensitivity values.

The introduction of a reducing gas such as hydrogen into the gas chamber provokes a decrease of the DC current. This result suggests that the effect of hydrogen is to passivate the active dangling bonds, perhaps through a screening mechanism as suggested by Steivenard et al. [11].

In addition, previous work reported a 10% recovery of photoluminescence on exposing a n-type Si sample to 325 mbar of H_2 after vacuum [12,13]. This recovery has been related to stabilisation of porous silicon dangling bonds. As a consequence, the H_2 gas increases the barrier height and thereby reduces the conductivity.

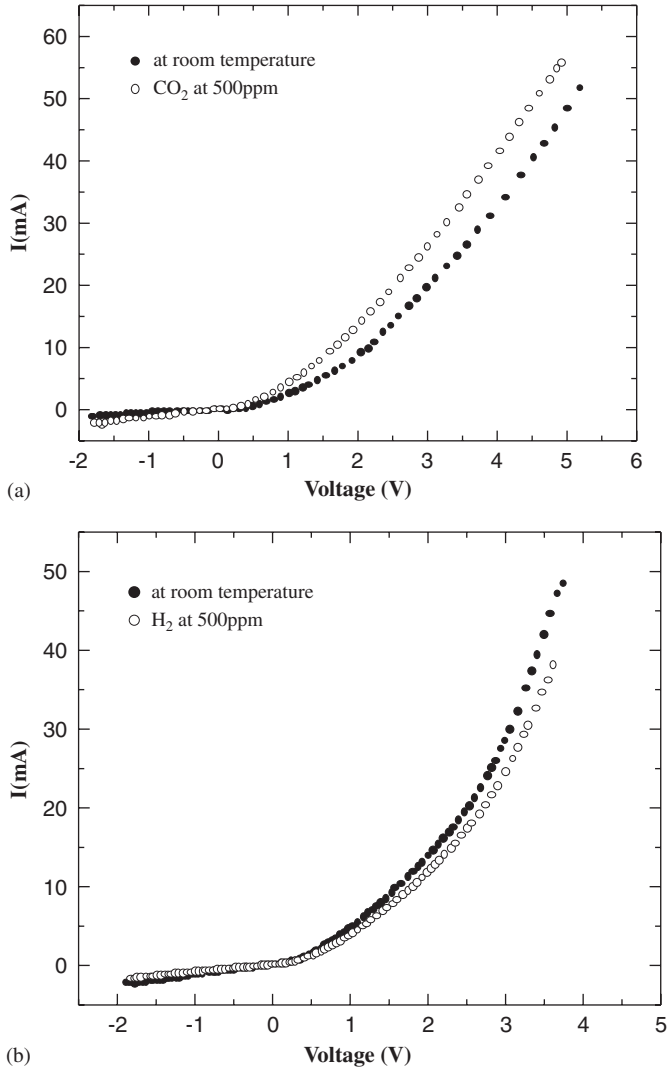

Fig. 1. *I–V* characteristics of a CH_x/PS/p-Si structure, for gases (a) CO_2 and (b) H_2.

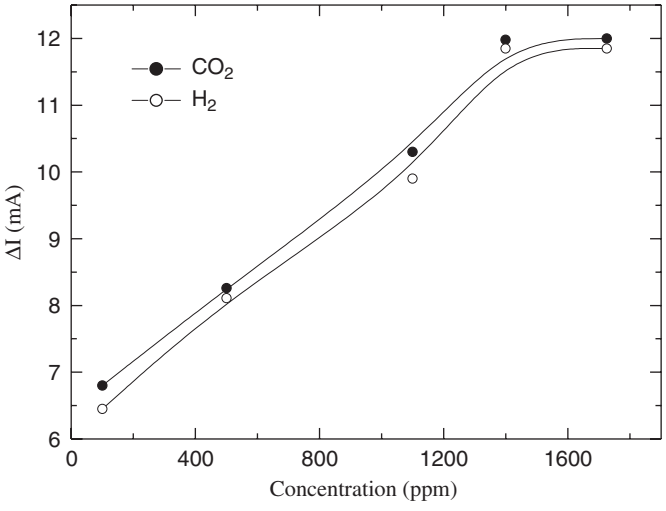

Fig. 2. Variation of current with gas pressure for the two gases, at 5 V applied bias.

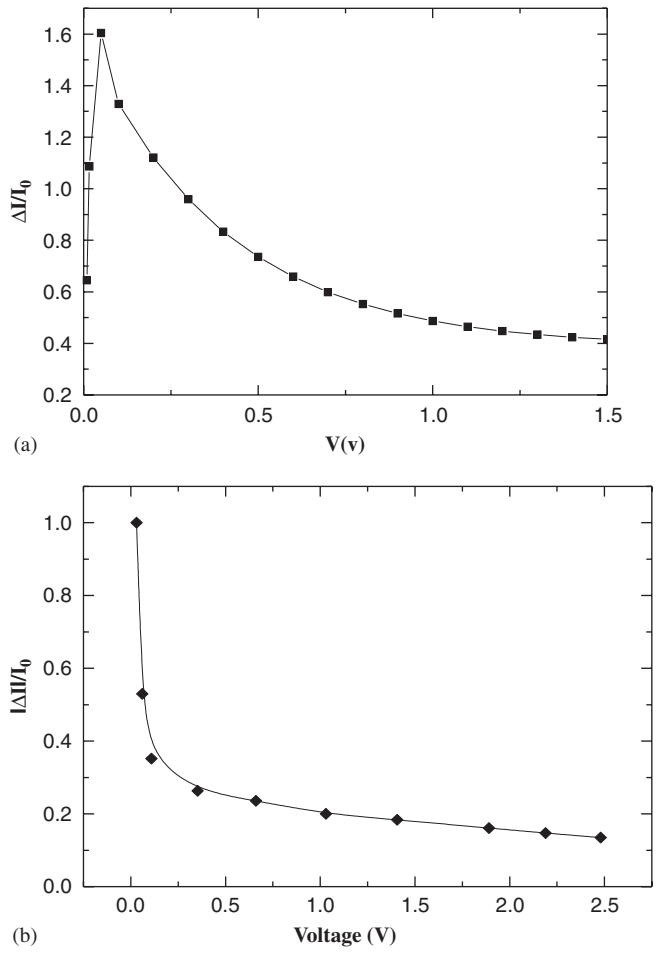

Fig. 3. Relative response of the current, as a function of polarisation for gases (a) CO_2 and (b) H_2 at 500 ppm concentration.

In addition to hydrogen we have checked the effect of oxygen. The interaction of porous silicon with oxygen has great relevance for any development of a sensor device because it normally has to work in the presence of the oxygen in air in order to detect any other gas. Fig. 4 shows the *I–V* characteristic of the sensor in an oxygen environment at a pressure of 1495 ppm. .The exposure to O_2 gas did not change the shape of the *I–V* dependence and also did not change the current magnitude at the fixed voltage. At the maximum applied voltage of +5 V, the variation of the current was about zero, indicating that the sensor is not sensitive to oxygen gas.

This feature indicates that our sensor can work easily in air without any influence of the oxygen environment and explains the high stability and nonoxidation of the sensor surface.

The dynamic response of the sensor towards two concentrations of CO_2 and H_2 gases at 3.5 V and at room temperature is presented in Fig. 5. A large current variation is observed. The current recovers rapidly and completely to the initial value. The response time is higher than the recovery time, indicating a slower rate for adsorption than for desorption of CO_2 gas from the CH_x/PS surface.

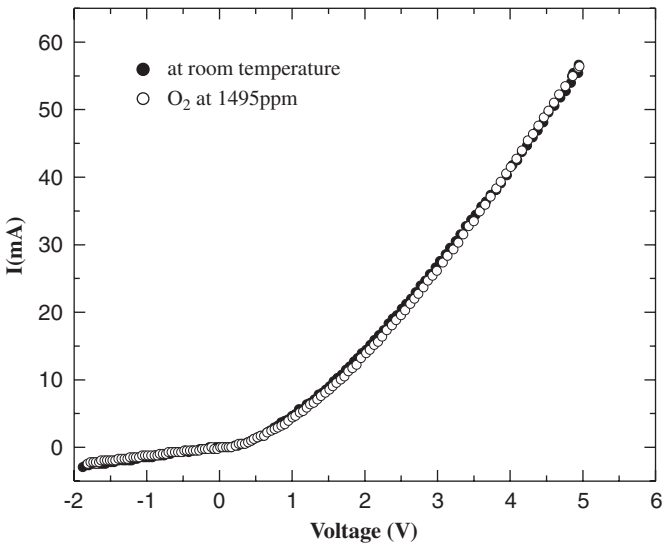

Fig. 4. *I–V* characteristics of a CH_x/PS/p-Si structure, at room temperature and under oxygen gas at pressure of 1495 ppm .

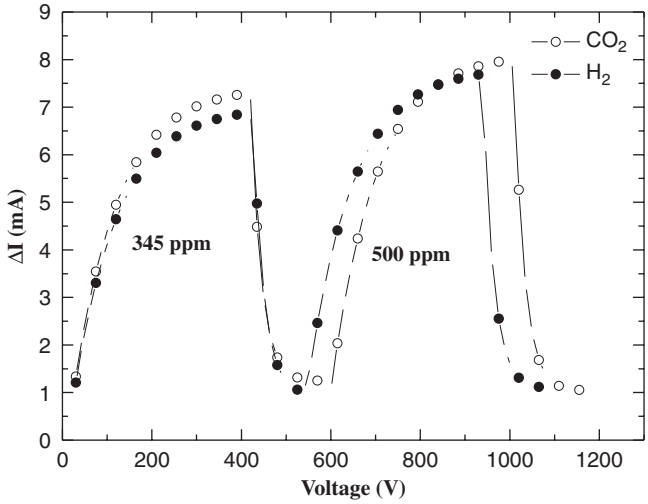

Fig. 5. Dynamic response of CH_x/PS/p-Si sensor to CO_2 and H_2 gases.

In this way, the sensor used in this work has been fabricated and tested over 18 months without any variation of the sensor characteristics indicating also a high lifetime of the CH_x/PS/p-Si device.

The dynamic response of the sensor towards a concentration of CO_2 gas at room temperature shows that large current variation is observed and the current recovers rapidly.

3.2. Capacitance measurements

The characterisation of the sensor is undertaken at 1 MHz. Fig. 6, which gives the variations of the capacitance versus bias voltage (*C–V*), shows that the introduction of the gases CO_2 (or H_2 not shown here) at 500 ppm pressure, induce a change in the capacitance–voltage values. One can

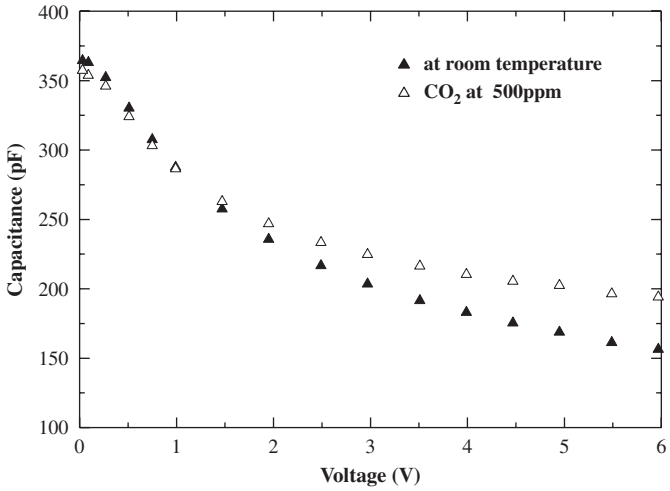

Fig. 6. Capacitance–voltage of a CH_x/PS/p-Si sensor measured at 1 MHz, for gas CO_2 at pressure of 500 ppm.

observe that the sensor behaves as a metal insulator semiconductor (MIS) structure. For the CH_x/PS/p-Si structure biased negatively, C decreases monotonically with bias voltage, for both gases. The high relative capacitance variations (ΔC) are shown for a bias voltage up to 1 V. However, the ΔC variation is positive for CO_2 and negative for H_2 gas, confirming the behaviour obtained on the I–V characteristics.

4. Conclusion

The results presented in this work show that the developed sensor responds to CO_2 and H_2 gas. However, the hydrogen gas interaction with the CH_x/PS surface is seen to be the result of an electrical screening whereas no variation in the current has been observed in presence of oxygen gas.

In addition, the developed sensor can operate at voltages in the 10–50 mV range demonstrating a high sensitivity.

References

[1] Gabouze N, Belhousse S, Cheraga H. Phys State Solidi (C) 2005;N9: 3449.
[2] He G, Narushima T, Iguchi Y, Goto T, Hirai T. 11th International conference on solid state ionics, Waikiki Beach, Honolulu, Hawaii, USA, 1997.
[3] Holzinger M, Maier J, Sitte W. Solid State Ionics 1997;74:217.
[4] Liu J, Weppner W. Solid State Commun 1990;76(3):311.
[5] Lee D-D, Chooi S-D, Lee K-W. Sensors and Actuators 1995;B25–26: 607.
[6] Kale GM, Davidson AJ, Fray DJ. Solid State Ionics 1996;86–88: 1107.
[7] Belhousse S, Cheraga H, Gabouze N. Sensors Actuat B 2004;100: 250–5.
[8] Ouchabane M, Tadjine R, Lahmar H, Zekara M, Henda K, Kessi O. Deposition of hard carbon films in triode RF (13.56 MHz) multipolar reactor from a methane plasma. In: Proceeeding of the 14th international symposium on plasma chemistry, Prague, Czech Republic, 1999. p. 1709.
[9] Cheraga H, Belhousse S, Gabouze N. Applied Surface Science 2004;495–500:238.
[10] Borgi K, Khirouni K, Mâaref H, Bourgoin JC. Eur Phys J Appl phy 1998;2:107–10.
[11] Stievenard D, Deresmes D. Appl Phys Lett 1995;67(11).
[12] Quercia L, Cerullo F, La Ferrara V, Di Francia G, Baratto C, Faglia G. Phys Status Solidi (a) 2000;182:473.
[13] Salonen J, Laine E. J Appl Phys 1996;80:5984.