

Effect of the surface sensing area in the response of porous silicon organic vapor sensors

G. GARCÍA SALGADO, T. DÍAZ, H. JUÁREZ, E. ROSENDO, R. GALEAZZI AND A. GARCÍA.
CIDS-ICUAP

UNIVERSIDAD AUTONOMA DE PUEBLA
14 sur y Blvd. Valsequillo, Edif. 137
PUEBLA, PUE. MÉXICO.
<http://www.buap.mx>

Abstract: In this work, the responses of porous silicon organic vapor sensors with different surface sensing area were investigated. Porous silicon layers with high specific surface area produced by electrochemical etching of p type 2-5 Ω -cm c-Si wafers were used to sense the presence of organic vapors (methanol, ethanol, isopropanol, xilene, acetone or water in this work). Different geometrical patterns of the metal front contact deposited by thermal evaporation and sensing areas were designed to determinate the influence of these parameters, keeping the same characteristics of the porous layer. The change of the electrical current was the parameter used to measure the response of the sensor in presence of the organic vapors applying a constant voltage of 5V. As a result we obtain important differences in the sensing curves, showing that the response of the sensor was not only dependent of the surface sensing area, but it was also found to be dependent of the metallic contact, wider metallic contacts gave us better responses even though the surface area and geometry of the porous layer exposed to the vapors was the same. The response in any case was better for methanol or acetone.

Key-Words: porous silicon, sensor, organic vapor.

1 Introduction

Porous silicon obtained by chemical or electrochemical dissolution of c-Si has shown a great quantity of applications and extensive works on this material has been reported both in the scientific and technological areas. The visible photoluminescence at room temperature of this material reported in 1990 by L. T. Canham has attracted considerable interest due to the possibility of manufacture an integrated optical device on Si [1,2]. The first develops of photovoltaic devices such as photodetectors and light emitting diodes has been reported [3-6]. Recently, an increasing interest on the sensing properties of PS material has emerged. Its ability to react with gases and sense them readily is related with the large surface to volume ratio [7]. The physical properties of PS samples, like the electrical resistance, have been observed to change in presence of humidity, organic vapors and contaminants like NO, NO₂, CO₂. The advantages of PS gas sensors compared with metal oxide gas sensors are; low cost, low power consumption and room temperature operation. This last fact is important due to the most of devices used for detection of ethanol using ZnO, SnO₂ or Bi₂(MoO₄)₃ exhibit sensibility temperature dependent being significant around 400-600 °C [8].

Another important advantage is the compatibility with silicon device fabrication technology.

The porous size has been classified like microporous (≤ 2 nm), mesoporous (2-50 nm) and macroporous (> 50 nm). The porosity, defined as the fraction of the apparent volume attribute to pores is larger for microporous. PS layers with high porosity have potential applications in light emitting diodes, anti-reflection coating and non-linear optics, medium porosity in micromachining, sensors and silicon on insulator, and low porosity in microcapacitors, wafer bonding etc [9].

One important parameter related with the sensing applications of porous silicon is the specific surface area; this is the accessible area of solid surface per unit mass of material. The values reported obtained using BET (Brunauer-Emmett-Teller) area measurements varies from <1 m² g⁻¹ in macroporous to 800 m² g⁻¹ in microporous material [9].

All those parameters are interrelated and they can be controlled changing the current density, electrolyte composition, resistivity and type of wafer in the fabrication process of the PS material.

In this work the study of PS organic vapors sensors with different geometry of the surface sensing area are presented, the change of electrical current of the sensor in presence of methanol, ethanol,

isopropanol, xilene, acetone or water vapors was measured.

2 Experimental procedure

Porous silicon layers were obtained by electrochemical anodization of p-type (100) c-Si wafers with 2-5 Ω -cm. As an electrolyte the HF acid diluted in ethanol (1:1) and current density of 30 mA/cm² was used, for such effect a teflon cell and constant current power source with 5-50 mA were designed, the cathode was implemented using 1 mm diameter tungsten wire. The set up used to obtain the porous silicon layers is showed in the Fig. 1. An aluminum film was deposited by thermal evaporation on the nonpolished face used like anode.

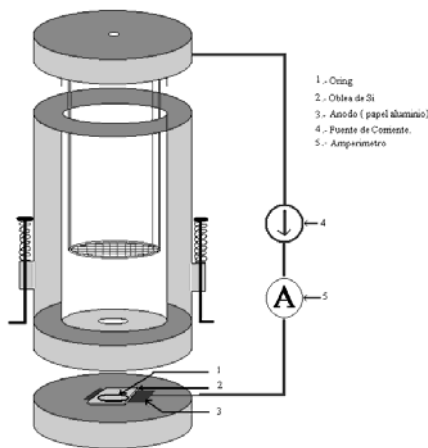


Fig. 1. Set up used to obtain porous silicon layer by electrochemical anodization.

To fabricate the sensors, 10 geometrical patterns were designed and transferred to stainless steel sheet by a photolithographic method, it was used like masks of an aluminum film deposited by thermal evaporation on the porous silicon layer, this film was used like electrical contact attaching copper wires with indium, the sensor device was introduced in a closed and hermetic reactor (Fig. 2) where nitrogen was used as a carrier gas of the organic vapor generated in a vessel containing the liquid solvent at room temperature, 100 cm³/min flow for the carrier gas was used and keep constant during the process. The change in electrical current was the parameter used to monitor the response of the sensor to acetone, methanol, ethanol, isopropanol, water or xilene vapors, the voltage applied for this measurements was 5 VDC. The change in electrical current of the sensing devices was measured using a DMM protek 506 connected to a personal computer. The set up for the sensing is showed in the Fig. 3.



Fig. 2. Hermetic reactor used to sense the response of the organic vapors.

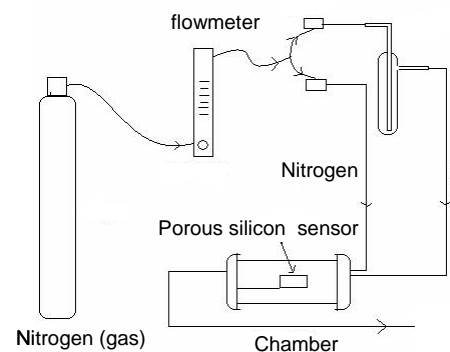


Fig. 3. Set up used for the sensing of the organic vapors

2 Results and discussion

The thickness, sensing area and specific surface area seems to be critical parameters to obtain the best sensing results, in our last work [10], we noted that thicker porous silicon layers produce slow responses and very thin porous silicon layers don't produce appreciable responses. The better sensing results were obtained for thickness around 5 μ m, in this work the thickness of the porous samples was 3.1763 μ m, it was obtained by a gravimetric method [9]. The specific surface area was of 895.5 m²/cm³, it was obtained as is described in [11] from comparison of bulk Si and porous silicon etch rates. Both parameters were keeping constants in the 10 sensor devices to compare only the effect of the surface sensing area. The designed patterns and response of the sensor devices to the presence of the organic vapors are showed in the Figs. 4, 5, 6 and 7.

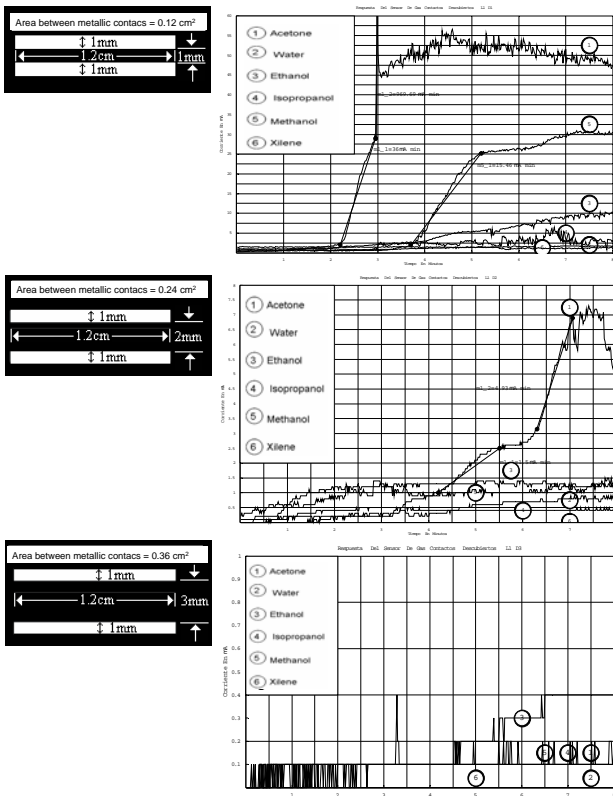


Fig. 4. Samples of porous silicon sensors, with a surface sensing of 12 mm of length and 1, 2 and 3 mm of wide, the metallic contacts have in all cases 12 mm² of area.

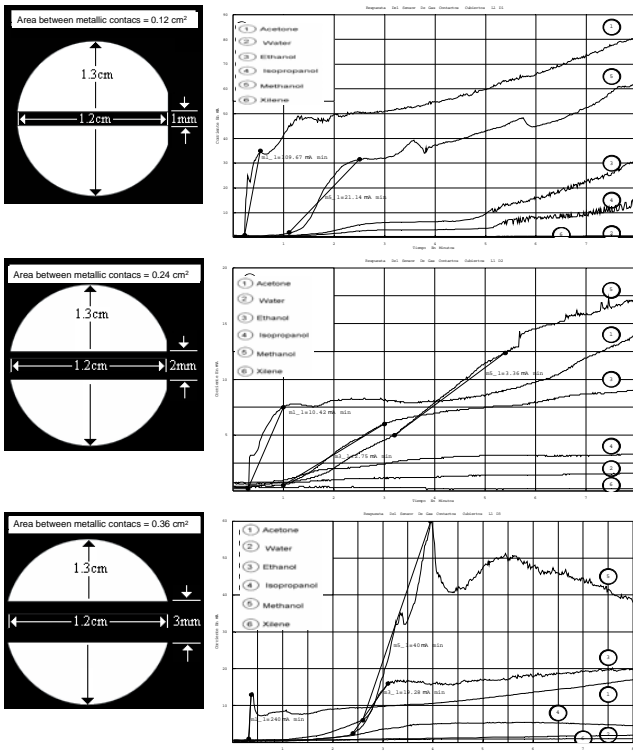


Fig. 5. Samples of porous silicon sensors, with a surface sensing of 12 mm of length and 1, 2 and 3 mm of wide, the metallic contacts have around 42 mm² of area.

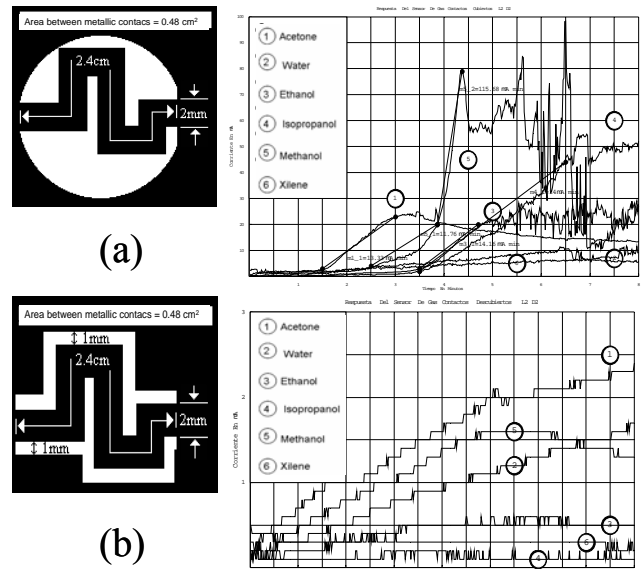


Fig. 6. Samples of porous silicon sensors, with a surface sensing of 24 mm of length and 2 mm of wide, the only difference is the area of the metallic contacts, one of them is wider than the other.

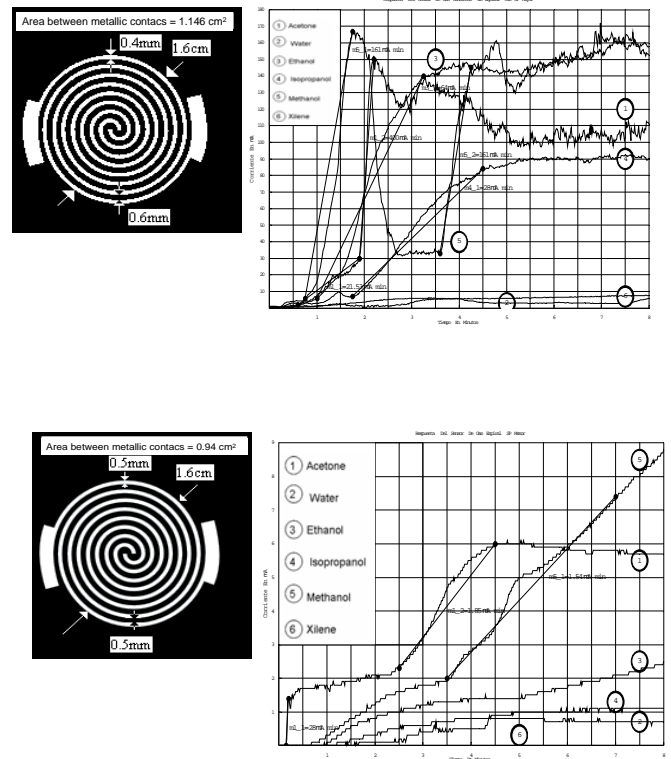


Fig. 7. Samples of porous silicon sensors designed to maximize the active surface area and keeping the metallic contacts at 0.5 mm and 0.6 mm of distance,

the active area was of 94.0 mm² and 114.6 mm² respectively.

In any case we can observe a better response for the acetone and methanol vapors, this fact is agree with another works, however we also can observe another phenomena:

If we compute the total inner area based in the effective surface area, we obtain that this is proportional to the active surface area (A_s); this is the area between the metallic contacts. Because of the thickness of the porous layer is the same in all the samples, taking account a specific surface area of 895.5 m²/cm³, and the thickness of 3.17 μm, the total inner area (A_i) will be:

$$A_i (\text{cm}^2) = A_s (\text{mm}) \times 28.387.$$

Therefore we have for the samples of the Fig. 4: 340.6, 681.2 and 1021.8 cm² of total inner area. We can appreciate that the better response corresponds to the smaller total inner area or active surface area, we suppose that in this case play an important role the physisorption process, the physisorbed molecules that arrive to the sensor have to cover the total surface area at least in one monolayer to form a way for the electrical current, therefore if we have a small separation between the contacts, the molecules cover the area faster and we obtain better responses for the sensor.

Another interesting phenomenon observed in the Fig. 4 is related with the dead time that appear in all cases, the response of the sensor is not immediate, and we can observe different dead times values for the organic vapors, this situation have to be also related with the speed of the molecules to cover the surface area, in all the responses the smaller dead time corresponds to the acetone vapor, follow for the methanol vapor. The quantity of molecules introduced to the reactor depends of two factors, the flow rate of the carrier gas and the vapor pressure of the organic solvents, in this work we used a constant carrier gas flow (100 cm³/min), therefore the vapor pressure will be the more important factor. The vapor pressures of the organic solvents used are showed in the table 1.

As we can see the acetone has the bigger vapor pressure and vapor flow, therefore the hitting of the molecules on the surface is greater. For the physisorption process the sticking coefficient is near to unit, therefore the quantity of physisorbed molecules have to be proportional to the vapor flow, for this reason we have smaller dead times for acetone, follow by the methanol and ethanol vapors. We can

observe this tendency in the curves of the Figs. 5, 6 and 7.

Solvent	Vapor pressure at 25 C (mmHg)	Organic vapor flow with carrier gas flow of 100 cm ³ /min	Dipole moment (Debye)
Acetone	221.99	41.26	2.88
Methanol	121.72	19.07	1.7
Ethanol	58.82	8.38	1.69
Isopropanol	45.16	6.32	1.85
Water	23.75	3.22	1.85

Table 1. vapor pressures at room temperature, flows and dipolar moments for the organic vapors used in this work.

Finally is showed in the Figs. 5 and 6a another interesting behavior, the sensors with wider metallic contacts has better responses even though the active surface area was the same that the sensors of the Figs. 4 and 6b respectively, in this case we suppose that play an important role the electric field and the dipolar moment of the molecules, as we can see also the dead times are smaller, therefore agree with the above discussion. We can suppose that the molecules arrive faster to the surface and fill the porous faster too, the wider metallic contacts produce a electric field in all the metallic zone and attract to the molecules with dipolar moment to the surface therefore the porous are filled faster and the dead time is smaller.

Using part of this conclusions were designed the sensors of the Fig. 7, where the active surface area was maximized and the round geometric pattern could enhance the electric field, we can observe a important difference with the first sensors, we have a good response inclusive for isopropanol. Water and xilene have very small vapor pressure and his response was negligible.

3 Conclusions

The effect of the surface sensing area in the response of porous silicon organic vapors sensors was investigated. The results show us that is very important a carefully design of the metallic contacts used for the devices. The distance between the metallic contacts is a crucial parameter for the fast response of the sensor, normally smaller surface sensing areas are related with faster responses. The wide of the metallic contact also has an important role in the response, the electric field produced for

this kind of contact enhanced the response of the sensors.

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