

# Gas sensitive porous silicon devices: responses to organic vapors

E. Galeazzo<sup>\*</sup>, H.E.M. Peres, G. Santos, N. Peixoto,  
F.J. Ramirez-Fernandez

*Sensores Integrados e Microsistemas, SIM Group, Laboratório de Microeletrônica, Escola Politécnica, Universidade de São Paulo (USP),  
Av. Prof. Luciano Gualberto, Trav. 3, 158, CEP 05508-900, Sao Paulo, SP, Brazil*

## Abstract

Geometrically scaled PS-based structures were fabricated in order to develop gas sensing devices by exploring porous silicon (PS) electrical characteristics. The electrical behavior of PS devices respond to polar organic vapors (as acetone and ethanol) reversibly in a reproducible way.

Devices were fabricated with three different perimeters, maintaining a constant area ( $5.76 \text{ mm}^2$ ) and constant PS porosity (60%) throughout samples, in order to evaluate their electrical impedance depending on the area/perimeter ratio.

Electrical impedance was measured from 10 kHz to 10 MHz in acetone, ethanol and vacuum (as reference) environments. The results obtained show the general aspect for impedance variation as expected for disordered materials such as amorphous semiconductors or polymers.

Measured impedance is fitted proportionally to  $(2\pi f)^s$ , where  $f$  is the excitation frequency. The exponential factor “ $s$ ” was found to be around  $-0.55$  for ethanol and  $-0.45$  for acetone, whereas in vacuum  $s$  equals  $-0.97$ , thus providing a method for identifying polar molecules. The parameter “ $s$ ” for the tested environments is independent of device geometry.

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**Keywords:** Porous silicon; Gas sensor; Organic vapors; Impedance; Acetone; Ethanol

## 1. Introduction

Porous silicon (PS) is obtained conventionally by anodization of silicon substrates. Crystallites of silicon formed by this means can present diameters varying from units of nanometers to tens of micrometers, depending on formation parameters (current density, electrolyte concentration, etching time, and substrate type). This characteristic, that is, the possibility of porosity control, makes PS suitable for several applications on gas sensing [1–5]. Its large internal surface area and high chemical reactivity with the environment further enhance the interest on sensing applications. Properties, such as photoluminescence (PL) and electrical conductivity, change when molecules are adsorbed to its surface [6,7], in such a way that these parameters may be monitored and related to physical reactions, to environmental conditions, or even to air quality, which makes porous silicon a promising material for a wide range of applications ranging from gas sensing to chemical detection in very small concentrations [8]. Despite PS sensitivity to humidity and high

concentration of organic vapor, problems such as stability, reversibility, and selectivity must be investigated, if it is to be applied as a commercially useful device. Some of these problems have been addressed before by our group [9] and other researchers [2], and we believe most of them are solvable by tuning anodization conditions, adapting masking alternatives, and proposing suitable models for PS formation and reactivity with the environment. In this paper, we specifically address this latter issue, and discuss possible applications by showing experimental results that confirm model predictions.

Stabilization of PS photoluminescent properties and minimization of electrical drift in the actual device are two important steps towards the fabrication of devices for characterization in reactive environments. Several processing sequences for PS surface passivation after anodization have been suggested in the past, in an attempt to deal with both issues. For example, Parkhrutik et al. analyzed the electrical drift of PS devices and attributed it to residual electrolyte inside the porous layers after anodization [10]. Taking into account previous reports as that one, the main objective of this work is to analyze the electrical behavior of PS devices during and after tests in environments with polar molecules, and to propose a model which relates the electrical response

<sup>\*</sup> Corresponding author.

E-mail address: [bete@lme.usp.br](mailto:bete@lme.usp.br) (E. Galeazzo).

URL: <http://sim.lme.usp.br>

to the environment, towards obtaining a reliable device for sensor applications.

In order to develop and to analyze the behavior of gas sensing devices by exploring PS electrical characteristics, geometrically scaled PS-based structures were fabricated which reversibly respond to organic vapors (in a reproducible way). We present the design, fabrication, characterization, and results when devices were submitted to acetone and ethanol as opposed to a controlled environment such as vacuum. Devices of oxidized PS were fabricated with three different perimeters, maintaining a constant area ( $5.76 \text{ mm}^2$ ) and constant PS porosity (60%) throughout samples, in order to evaluate their electrical impedance depending on the area/perimeter ratio.

This analysis will be presented taking into account that the electrical impedance of PS devices depends on applied frequency of measurement and on contact geometry on its surface, as reported in the literature [11].

## 2. Experimental details

### 2.1. Device fabrication

Devices were fabricated in silicon substrate type p,  $\langle 100 \rangle$  orientation and  $14 \Omega \text{ cm}$  resistivity. PS layer was formed on a  $7.55 \text{ cm}^2$  area through the conventional anodization process, with  $J = 20 \text{ mA/cm}^2$  for 10 min in a solution of HF (48 wt.%) and ethanol (1:1). After anodization, samples were submitted to chemical oxidation in solution of  $\text{HNO}_3$  66% for 15 s, as a way of stabilizing the surface

Table 1  
Area/perimeter ratio of rectangular contacts (length  $\times$  width) of Al/PS/Si/Al devices

| Device | Length (mm) | Width (mm) | Area ( $\text{mm}^2$ ) | Perimeter (mm) | Area/perimeter ratio ( $\text{mm}^2/\text{mm}$ ) |
|--------|-------------|------------|------------------------|----------------|--|
| D11    | 2.4         | 2.4        | 5.76                   | 9.6            | 0.60   |
| D12    | 4.8         | 1.2        | 5.76                   | 12             | 0.48   |
| D2     | 7.2         | 0.8        | 5.76                   | 16             | 0.36   |

and reducing possible reactions with the ambient [9,12]. The porosity of PS as formed is  $(61 \pm 3)\%$ , measured by the gravimetry method. A second sample with PS, formed in the same conditions of the other devices, was fabricated in order to monitor the evolution of the superficial chemical bonds during the experimental runs.

Electrical contacts were formed by Al thermal evaporation ( $\sim 500 \text{ nm}$ ) onto PS surface. The restrictions of dimensions on devices were given by the limitations of fabrication processes, since a shadow mask was used for definition of rectangular aluminum contacts on the porous layers. The area/perimeter ratio of the devices analyzed in this work is shown in Table 1. Fig. 1 presents a schematic cross section of a device with electrical contacts.

### 2.2. Gas exposure and measurements

Fig. 2 illustrates the experimental set-up used to measure PS sensors. All electrical measurements were performed at room temperature ( $25^\circ \text{C}$ ) in a sealed chamber controlling

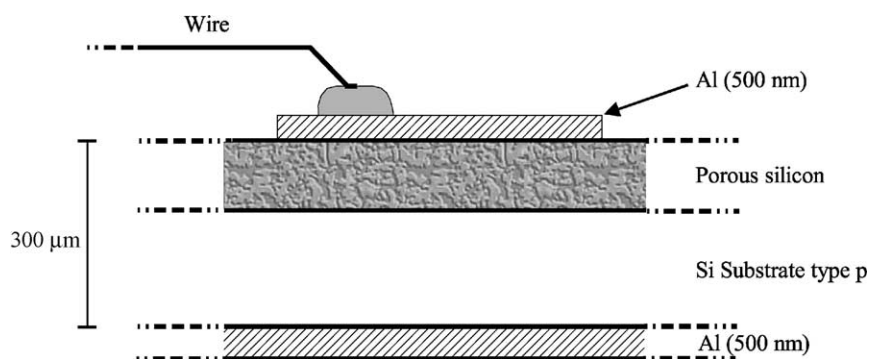


Fig. 1. Cross-section of Al/PS/Si/Al device with electrical contacts.

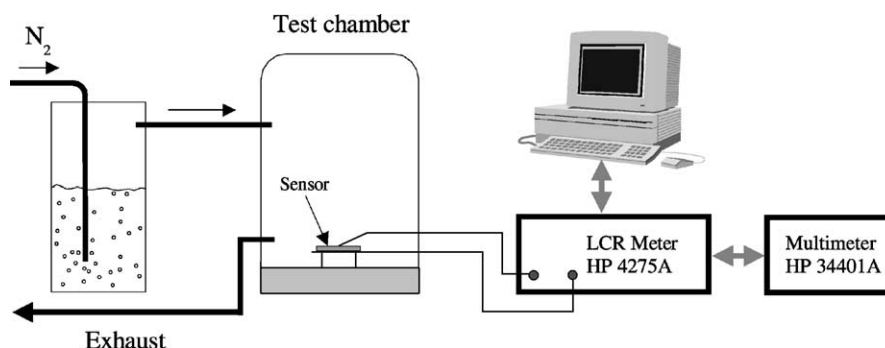


Fig. 2. Schematic diagram of the experimental set-up for sensor measurements.

different kinds of gaseous atmospheres. Devices were submitted to test in saturated ambient of acetone and ethanol vapors. Nitrogen was used as carrier gas (0.1 l/min) and it was saturated with vapor by passing it through the solution containing the chemical substance under study, as depicted in Fig. 2. In order to promote desorption of chemical elements infiltrated in the pores, samples were submitted to controlled atmospheres within a climatic chamber model Tenney Ten (Tenney Engineering, Inc., NJ, USA) at 80 °C and 20% relative humidity for 1 h after each data acquisition. Samples were maintained in vacuum afterwards, in order to guarantee they were free from adsorbed species.

A multi-frequency LCR Meter model HP4275A (Hewlett-Packard, Palo Alto, CA, USA) was used to simultaneously measure impedance and capacitance of the sensors with the same levels of dc and ac polarization. An HP 34401A multimeter (Hewlett-Packard, Palo Alto, CA, USA) was used to monitor the polarization of the devices. Each impedance measurement cycle swept ten strips of frequency successively from 10 kHz to 10 MHz, lasting about 100 s. A virtual instrument was developed in LabVIEW® (National Instruments, Austin, TX, USA) to control equipment and manage acquisition data. Recordings were performed during a period from 60 to 180 min, while devices were polarized with 1 V dc (reverse polarization with saturation current approximately 10 pA) and 500 mV ac (peak). During acquisition, samples were maintained at room temperature, at constant relative humidity and without external illumination.

Chemical characterization was performed by Fourier transform IR analysis (FTIR), both before and after gas

exposure. A FTS-40 spectrometer (Bio-Rad Laboratories, Hercules, CA, USA) with a resolution of 2 cm<sup>-1</sup> was used for all FTIR analyses.

### 3. Results and discussion

Devices and PS test samples were stored in air during several months before the beginning of gas testing. The chemical bonds of a PS surface test sample (passivated by chemical and natural oxidation and maintained with the devices in the test chamber), were monitored by means of FTIR analysis in the absorption condition during gas testing.

Electrical characterization of the devices was carried out for about 6 months in several gaseous atmospheres conditions saturated with acetone and ethyl alcohol. During this period, FTIR absorption spectra of one sample were measured before the experiments, after the exposition in saturated atmosphere and after desorption of porous layer. Little change on surface was observed both in energy and intensity in the resultant spectra, as illustrated by Fig. 3. This shows that the oxidation condition to which devices were submitted induces a reliable passivation of the exposed surfaces. These spectra are typical for PS samples with high oxidation degree [13,14].

Figs. 4 and 5 show the stationary electrical behavior (impedance versus frequency) of devices D2, D11 and D12 in vacuum and after long time exposure (about 3000 s) submitted to concentrated acetone vapor and concentrated ethanol vapor, respectively. The devices change their elec-

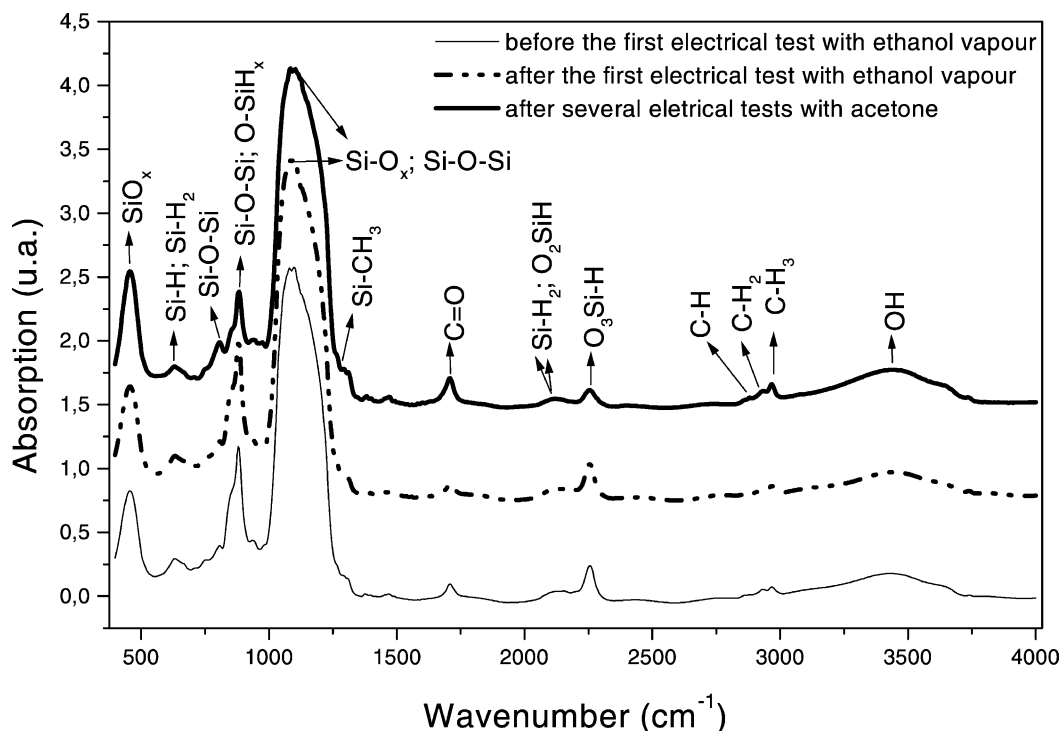


Fig. 3. FTIR analysis of PS before and after electrical measurements in saturated environment with polar molecules.

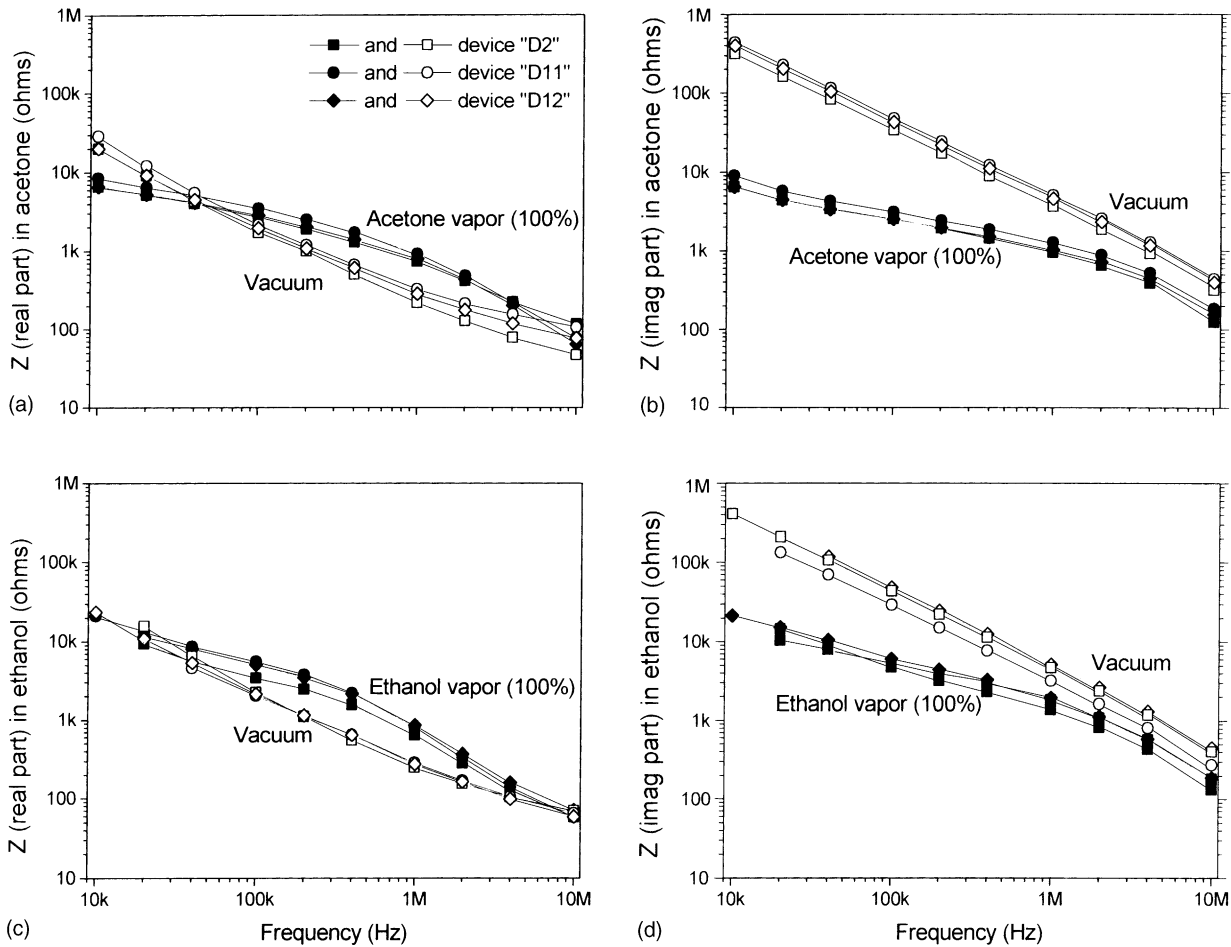


Fig. 4. (a) Impedance vs. frequency curves for devices D2, D11 and D12. (a, b) Real and imaginary part for concentrated acetone vapor environment; (c, d) real and imaginary part for concentrated ethanol vapor environment. Curves for vacuum are also shown for comparison.

trical response to concentrated vapors but no critical variation is observed between devices within the same experiment, although the contact geometries have different area/perimeter ratio. It is worth noting that all devices presented reversible electrical response after the desorption process. Control measurements were taken in vacuum.

Fig. 5a and b illustrate real and imaginary components of the impedance versus frequency for sensor D2 in vacuum as well as after long time exposure in atmospheres saturated with five different acetone partial pressures (after 3000 s). Six test conditions were chosen for the essays: 100, 50, 20, 10, 5 and 1% of acetone dissolved in aqueous solution. Not

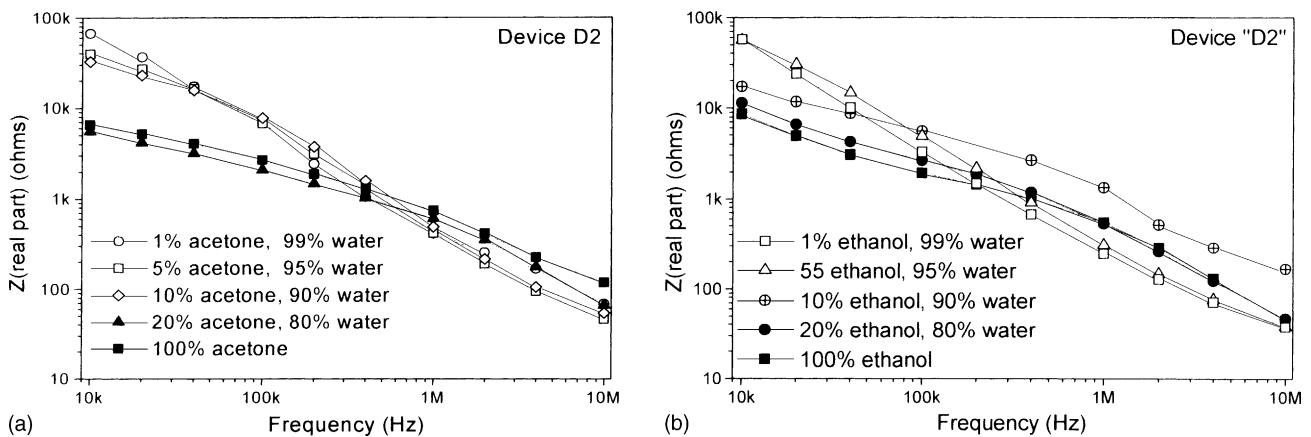


Fig. 5. (a) Real part of impedance vs. frequency of device D2 during tests with different acetone concentrations; (b) real part of impedance vs. frequency of device D2 during tests with different ethanol concentrations.

only does the absolute intensity of impedance (real and imaginary part) change during the tests, but also the slope of these curves changes with concentration.

The relationship between frequency and electrical resistance (real part of impedance) in devices submitted to desorption processes of chemical residues or vacuum can be fitted by an expression given by:

$$Z'(\omega) \propto \omega^s \tag{1}$$

where  $Z'$  is the real part of the impedance and  $\omega$  ( $2\pi f$ ) the measured angular frequency. The law presented is considered a universal law which governs disordered materials such as PS [15]. The exponential factor “ $s$ ” ranges from  $-0.95$  to  $-0.99$ . This parameter is calculated from experimental data in the range from 10 kHz to 4 MHz when devices are in vacuum.

The dependence between frequency and resistance was characterized for all fabricated devices (D2, D11 and D12) submitted to vacuum before exposure to vapor and after desorption processes.

In the obtained curves for resistance versus frequency for the devices submitted to atmospheres saturated with polar molecules (that is to say, acetone and ethyl alcohol), the same exponential relationship described in the expression (1) is observed. However, the value of the exponent “ $s$ ” in this case varied, depending on type of molecules adsorbed and on the concentration of these molecules in vapor environment, presenting modulation of this parameter during the essay.

Fig. 6a and b show the dependence of exponent “ $s$ ”, calculated from the slope of the linear portion of the graphs

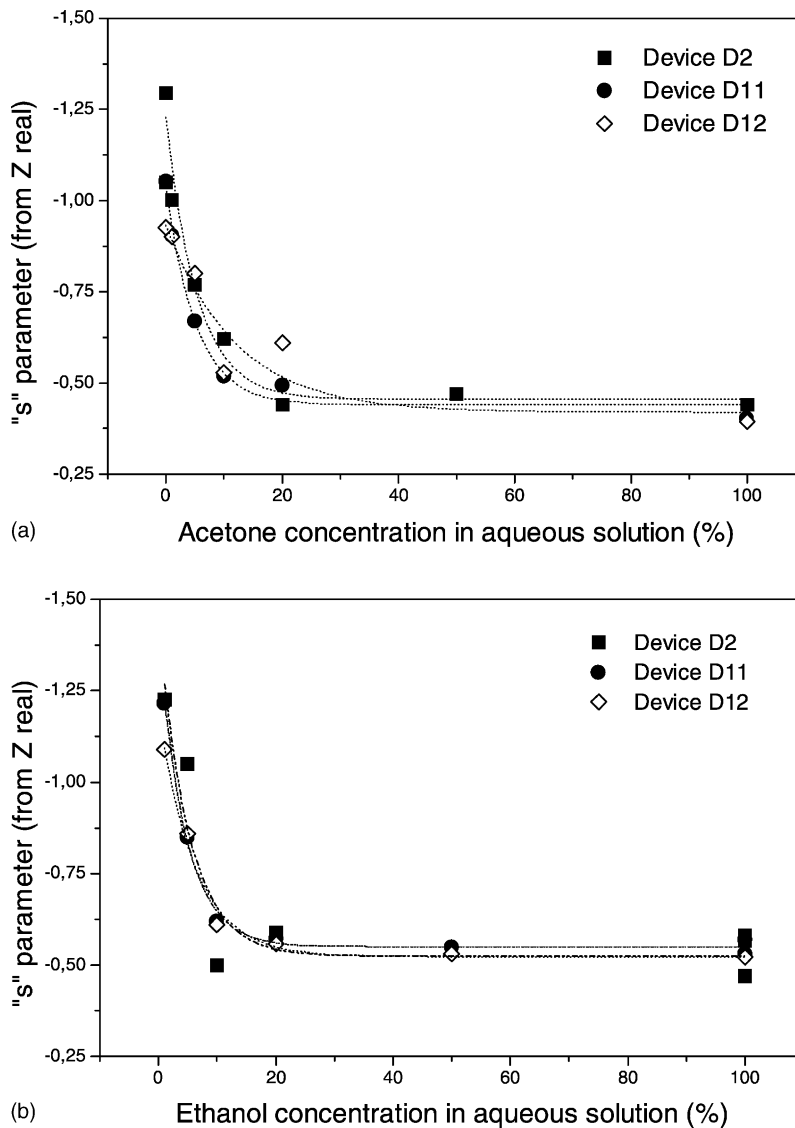


Fig. 6. (a) Variation of  $s$  depending on acetone concentration (% volume in  $H_2O$ ). There is no significant difference among devices (D2, D11, D12), showing that  $s$  is not correlated to geometry in the case of acetone. The exponential decay is clear from experimental data, and it happens for all tested devices; (b) parameter  $s$  as evaluated for different ethanol concentrations (5–100% in  $H_2O$ ). For each concentration, the value of  $s$  is plotted for three devices. There is no variation of  $s$  within devices, although all curves present exponential decay with increasing ethanol concentrations.

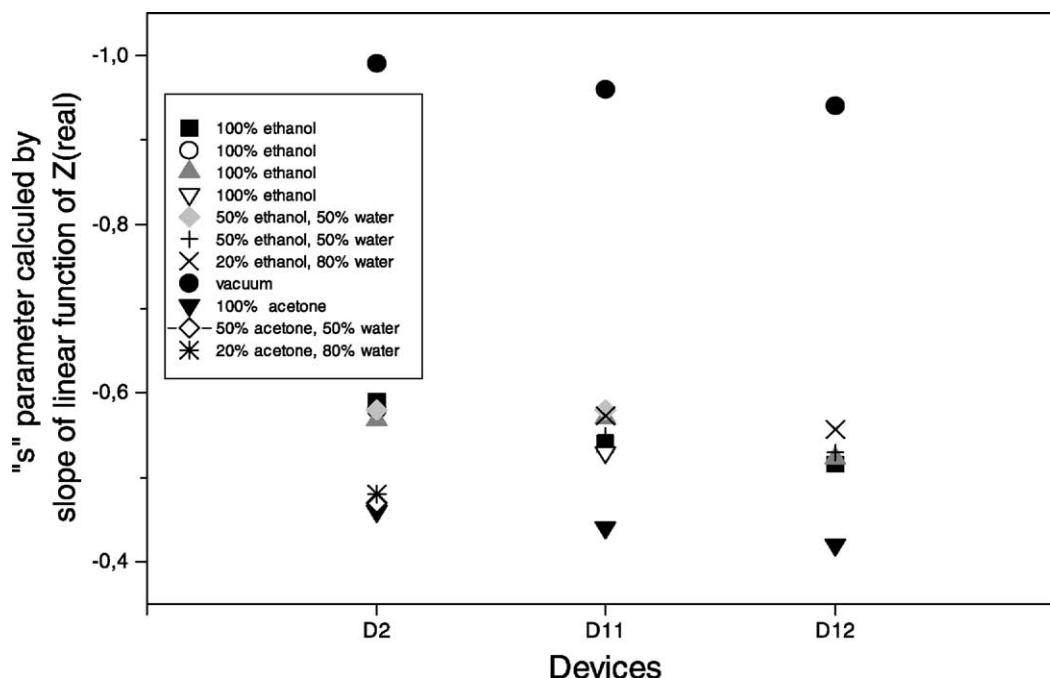


Fig. 7. Comparison of parameter  $s$  for devices with different area/perimeter ratio. For each device,  $s$  is evaluated based on experimental results. Modulation of  $s$  is obtained through the effect of polar molecules, such as ethanol ( $s = -0.6$ ) and acetone ( $s = -0.54$ ), as opposed to the behavior in vacuum ( $s = -0.9$ ).

(real part of  $Z$  on frequency measurements, in the range from 10 to 400 kHz), in different acetone and ethanol vapor concentrations. The behavior of all devices is similar (no variation of parameter “ $s$ ” is observed for all devices for measurements performed between 20 and 100% of ethanol or acetone in aqueous solutions), but “ $s$ ” is distinct for ethanol, acetone and vacuum. No influence of water vapor was observed on the response of sensors to organic vapors in these gaseous mixtures.

The non-linear behaviors in frequency and impedance of devices is accentuated in adsorption processes corresponding to the experiments accomplished with saturated atmosphere of acetone and ethanol. In processes saturated with acetone, “ $s$ ” is  $(-0.45 \pm 0.02)$  (see, for example, Fig. 7). Comparatively, the value of “ $s$ ” remained approximately constant at  $(-0.53 \pm 0.01)$  to  $(-0.56 \pm 0.01)$  for essays in atmosphere saturated with ethanol. As already mentioned, the initial relationship between the electrical resistance and the frequency is re-established after desorption of gaseous substances in the devices, the results being very close to the measured conductivity obtained before each test. One can suppose that PS layers neither react chemically with the molecules, nor react with any residue of the electrolyte which could be trapped in the pores.

A possible interpretation for these results is based on the microstructure of the PS: the ac electrical conduction of PS is associated with the hopping transport of charge carriers through a high disordered network of PS, among localized sites, whose transition rate depends both on the spatial distance and on the energy difference between the two sites involved. It is assumed that polar molecules, as adsorbed by

PS, might lower energy barriers between sites or particles, thus enhancing conductivity.

The devices tested presented long response time (about thousands of seconds), which may be attributed to the thickness of the PS active layer, approximately  $10 \mu\text{m}$ , and to the large area of the devices (data not shown).

Sensitivity increases with perimeter, as shown here by D2 and D11, for example, suggesting that the adsorption and desorption reactions are occurring on the device edges. Further evidence to this hypothesis can be provided by capacitive measurements and by increasing the number of tested devices. This is the subject of our current investigations. Preliminary results show that capacitance may be the variable of choice for analyzing device response depending on area/perimeter ratio.

#### 4. Conclusions

Porous silicon-based devices have been exposed to two different substances with polar molecules (acetone and ethanol) along with control environmental conditions (vacuum). The devices could be repeatedly used and tested in different atmospheres, thus proving that the adsorption and desorption processes on the PS surface take place in a reversible and reproducible way. A respective change in impedance has been observed, depending on excitation molecule. A model for impedance variation has been proposed and used to fit experimental data. Modulation of the parameter “ $s$ ” showed that identification of polar molecules is possible in the case of ethanol and acetone.

The analysis of the mechanism for the sensors response is subject of our current investigations. It is clear that different gases accordingly elicit different sensor responses, and from the same experiments we have observed that the aging process modulates the characteristic impedance response.

To sum up, it was verified that electrical properties of PS devices change reversibly when submitted to organic vapor atmospheres. Additionally, the fabricated devices do not respond to nonpolar molecules such as oil gases or in control experiments with gases such as nitrogen (data not shown). The proposed model for analyzing impedance variation with frequency accounts for the experimental modulation observed, and supports the hypothesis of gas selectivity for devices fabricated with porous silicon as base material.

### Acknowledgements

This work was partially supported by Program RECOPE/FINEP ref. 77/97/0481/00, sub project Sensors and Actuators 3.856/96. Gerson dos Santos would like to thank CNPq for financial support. We would like to thank Maurício O. Perez Lisboa (USP, Brazil) and Dosil Pereira de Jesus (USP, Brazil), respectively, for valuable help with LabVIEW instrumentation and the presentation of this work in IMCS'9th.

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### Biographies

*Elisabete Galeazzo* obtained her Degree in Physics from the Universidade de São Paulo in 1989. She has been a researcher at the Laboratório de Microeletrônica of Escola Politécnica da Universidade de São Paulo since 1990, where she received a MS degree in 1993 and her PhD degree in Electrical Engineering in 2000. Her current research is focused on the development of porous silicon gas sensors and microfabrication technologies using porous silicon.

*Henrique Estanislau Maldonado Peres* received his BS degree in Physics in 1990 and obtained his MS degree in Electrical Engineering in 1996, both from Universidade de São Paulo. Now, he is working towards his PhD degree investigating the fabrication of microstructures and integrated sensors. He works at the Sensores Integráveis e Microsistemas group in the Laboratório de Microeletrônica of Escola Politécnica da Universidade de São Paulo, Brazil. His research interest includes microelectronics processing, MEMS and sensors integration.

*Gerson Dos Santos* was born in 1977, São Paulo, Brazil, he obtained his degree in Microelectronic Technology from FATEC—Faculdade de Tecnologia de São Paulo in 2000. His initial work in 2000 was “Analysis and Design of Power Sources to Microwave Devices” developed in CTMSP—Centro Tecnológico da Marinha em São Paulo. His current research towards his Master degree is focused on the development and design of porous silicon gas sensors technologies using porous silicon as active layer.

*Nathalia Peixoto* received her BS and MS from Unicamp, Brazil, and her PhD from USP, Brazil, all in electrical engineering. She worked with the spreading depression phenomenon, then contributed to the German retinal implant project, and finally developed microelectrode arrays for cell cultures. She is currently a post-doctoral researcher at Stanford, CA, USA, investigating microfabricated oxygen sensors for cardiac cell cultures.

*Francisco Javier Ramirez-Fernandez* is associate professor, Universidade de São Paulo, SP, Brazil. He is electrical engineer (1970) from UTE Santiago, Chile, MS and Doctor in Microelectronics (1978 and 1986) from USP, Brazil. He is Vice-Head of the Microelectronic Laboratory LME/EPUSP. He is also Head of Integrated Sensors and Microsystems Division. His technological development include: bipolar low power transistor, operational amplifier, voltage regulators, integrated injection logic, high power integrated circuits technology, BIFET technology, VLSI magneto transistor, Pd-MOSFET gas sensors, porous silicon technology, electronic nose and neuro-electronic arrays.