Analysis of Porous Silicon Devices for Gas Sensors

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Abstract
In this work the results obtained to develop gas sensor built with porous silicon (PS) are presented, showing the influence of organic vapors such as acetone and ethanol on electrical characteristics of devices made of Al/PS/Si/Al.

The sensitivity of the PS was characterized observing changes in capacitance as a function of frequency by means of devices geometrically scaled according to perimeter/area ratio. The relationship between each organic substance and the variation of impedance with frequency was obtained, verifying that the performance of devices is not shifted by the test conditions. The behavior of complex impedance is typical of a disordered material. Also, through FTIR measurements, there is no evidence of change of PS structure due to a direct adsorption of gases, showing that the passivation of PS devices is effective to block the action of chemical substances in interface states.

1. Introduction

Porous silicon (PS) is a very interesting material in the field of gas sensors due to its high specific surface (a few hundreds of square meter per cubic meter) and reactivity to the environment, as well as for its compatibility with conventional silicon technology [1,2]. Its high specific superficial area and susceptibility to chemical action of elements on its surface facilitate the exploration of effects provoked by the adsorption and desorption of chemical substances including, among others, changes of refractive index [3], photoluminescence [4-8] and mainly electrical conductivity [5,9]. Moreover the characteristics of PS are strongly dependent on the environmental conditions to which they are submitted to such as humidity [6,10] and organic chemical vapors [2], besides chemical or thermal treatments made after anodization [11,12].

KOSHIDA et al [13] were one of the first to present results obtained from impedance measures in the anodization processes of the PS in order to study its formation mechanisms. This technique was also applied to detect residues of the electrolyte inside the pores in the first times of recently formed layer [14,15]. Other contributions of a.c. conductivity characterizations in layers of PS found in the literature are oriented to model the phenomenon of transport of electric charge carrier that happens in PS [16-18].

The main objective of this work is to contribute to the characterization of electrical conductivity of PS, analyzing the behavior of structures metal/PS/Si/metal submitted to different gaseous atmospheres (acetone and ethanol vapor) by means of impedance analysis [19]. The characterization of the evolution of the chemical species in the PS surface is made by means of FTIR technique.

2. Fabrication of test devices

Devices were manufactured in silicon substrate type p, orientation <100> and resistivity of 14 Ωcm. The layer of PS was formed in an area of 7.55 cm² through the conventional anodization process, with J = 20 mA/cm² for 10 minutes in HF and ethanol solution (1:1). After anodization, the sample was submitted to a chemical oxidation in solution of HNO₃ 66% for 15 s, as resource to stabilize its surface and reduce possible reactions with the ambient [12,20]. The porosity of the PS as formed is (61 ± 3)%, measured by gravimetry method. A second sample, formed in the same conditions, was fabricated to monitor the evolution of superficial chemical bonds during the experiences.

Devices were formed by Al evaporation (~500 nm) onto PS surface. The restrictions of dimensions on devices were given by the limitations of fabrication processes, since mechanical mask was used for definition of aluminum contacts on the porous layers. The perimeter/area ratio of the devices analyzed in this work (named D2 and D11) is shown in Table 1.

Figure 1 presents a cross section of a device with the electric contacts. The sensors testing system is shown in Figure 2. All electrical measurements were performed at room temperature in a chamber controlling different type of gaseous atmospheres. The devices were submitted to test in saturated ambient of acetone and ethanol. The injection of gas substances into testing chamber was accomplished by bubbling of continuum nitrogen flux (0.1 l/min) in one recipient with chemical substance in liquid state. To promote the desorption of chemical elements infiltrated in the pores, the samples were submitted to controlled atmospheres in a climatic chamber Tenney, with temperature of 80°C and relative humidity of 20% for one hour after each data acquisition. The samples were maintained in vacuum after end each experiment.
Table 1: Area/Perimeter ratio of rectangular contacts (length b and c) of Al/PS/Si/Al devices

<table>
<thead>
<tr>
<th>Disp.</th>
<th>Length b [µm]</th>
<th>Length c [µm]</th>
<th>Area [µm²]</th>
<th>Perimeter [µm]</th>
<th>Area/Perimeter ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>D11</td>
<td>2.400</td>
<td>2.400</td>
<td>5.76E+6</td>
<td>9.600</td>
<td>600</td>
</tr>
<tr>
<td>D2</td>
<td>7.200</td>
<td>800</td>
<td>5.76E+6</td>
<td>16.000</td>
<td>360</td>
</tr>
</tbody>
</table>

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

Fig. 2. Schematic diagram of test chamber with measurement system.

A Multi Frequency LCR Meter (HP4275A) was used to measure impedance and capacitance of sensors at the same time, preserving the same gaseous atmospheres and with the same levels of dc and ac polarization. An HP 34401A multimeter was used to monitor the polarization of the devices. Each cycle of impedance and capacitance measure, sweeping ten strips of frequency successively from 10 kHz to 10 MHz, lasted about 100 s. A virtual instrument was developed through Labview® to manage equipments and acquisition data. The measurements were performed during a period from 60 to 180 minutes, and the devices were polarized with 1 V dc (reverse polarization and ≈10 pA of saturation current) and 500 mV ac. During the acquisition, the samples were maintained at room temperature without light.

The IR analysis was achieved before and after the excitation on gas vapor by using a Bio-Rad Fourier transform IR spectrometer (model FTS-40) with 8 cm⁻¹ of resolution.

3. Experimental results

Figure 3 shows real and imaginary components of the impedance vs. frequency for sensor D2 as in vacuum as after long time exposure in atmosphere saturated with molecules of acetone (about 3000 s). Figures 4 and 5 show the impedance dependency of the devices on the time after injection of acetone and ethanol saturated atmospheres. One can see that approximately after 2000 s the injection of chemical substances the devices stabilized in new electric condition. Experimental results obtained for acetone are the most significant with the largest sensibility available. However, the transition from a vacuum condition to an atmosphere including polar molecules is a very slow process and should be optimised.
The little dependence of the capacitance in function of frequency from 10 kHz to 10 MHz it was accentuated considerably in the electric test made with composed gases by polar molecules. Figure 6 shows the variation of at least an order of magnitude of capacitance versus frequency of device D2 during exposition to acetone ambient.

This variation can be related to the modification of the average dielectric constant of the PS layer in the presence of these molecules. Figures 7 and 8 show the long time for the devices to be stabilised in another equilibrium condition, but sensitivity is high both for acetone and ethanol atmospheres.

PS surface on the substrate with the devices and the test sample were previously treated with HNO3 oxidation and exposed to environment during several months before beginning the gas testing. The sample test was maintained in the same environment conditions of the devices and its chemical surface was monitored by means of FTIR analysis in the absorption condition. The evolution of this surface, passivated by chemical and natural oxidation, is shown in Figure 9 and Figure 10 for all tests performed.

During natural aging process, an increase of the absorption bands related around 1000-1250 cm\(^{-1}\) (corresponding to the asymmetric stretching region of SiO\(_x\) and Si-O-Si) [21-23] and around the vibration mode at 870 cm\(^{-1}\) (regarding the connection of the type
SiH$_2$O$_x$) [24]. Peaks at 2090, 2125 and 2140 cm$^{-1}$ (identified as Si monohydride, dihydride and trihydride stretching modes respectively) [25] are reduced during the samples aging process and bands at 2200 and 2250 cm$^{-1}$, attributed to Si-H stretching modes backbonded to oxygen atoms, are increased [22,26]. After initial analysis of the devices in several saturated atmospheres of vapour, acetone and ethanol, the samples presented superficial chemical bonds modified, due to a high oxidation degree. The increase of absorption intensity due to SiO$_2$ vibration modes stands well out in 456 cm$^{-1}$, among 1000-1200 cm$^{-1}$ due to vibration modes of SiO$_x$ and Si-O-Si and in the strip of 880 cm$^{-1}$, related to the stretching modes respectively) [25] are reduced during the samples aging process and bands at 1700 cm$^{-1}$ and 2960 cm$^{-1}$ corresponding to C-O and C-H, bonds can be observed probably due to the contamination of surface because of samples manipulations and due to the reaction of surface with atmospheres saturated with organic molecules [23,27]. The presence of a fine absorption band around 3500 cm$^{-1}$ is also noticed, associated to the groups "silanole" (SiOH) [28].

The electric characterisation was carried out for about two months in several gaseous atmospheres conditions saturated with acetone and ethyl alcohol. During this period, absorption spectra for FTIR of one sample test were measured before the experiments, after the excitement 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 prove that this oxidation condition is a good passivated surface (see Figure 10).

One of the factors of long response time (around 2000 - 3000 s) of the devices is attributed to the thickness of the porous layer. Little change on surface was observed both in energy and intensity in the resultant spectra, as prove that this oxidation condition is a good passivated surface (see Figure 10).

![Fig.10. FTIR analysis of PS before and after electrical measurements in saturated ambient with polar molecules.](image)

It can be concluded that the change of electric behavior of devices was only owed to the effect of adsorption of the molecules, not being detected changes of the superficial chemical connections during the experiments. This measure of FTIR becomes useful complement to the electric characterizations made after the desorption processes, which showed reversion of its electric response in vacuum after excitation. Samples of PS with strongly oxidised surface shown sufficient performance to be used as gas sensor. However, the initial chemical oxidation made with HNO$_3$ is not an efficient passivation process yet. So, this process needs more investment to be optimised.

4. Discussion and conclusion

In the Al/PS/Si/Al devices analysed it was concluded that capacitance (C) is larger and the impedance (Z) it smaller in gaseous atmospheres containing polar molecules than in vacuum. It was also observed that both the capacitance and the resistance are reversible with regard to the atmosphere of test. The relationship between electric resistance and frequency in these devices submitted to desorption processes of chemical residues, it is given for:

\[ Z'(\nu) \alpha \nu^s \]  

where $Z'$ is the real part of the impedance, $\nu$ it is the measured frequency, and the exponent "s" is calculated from -0,90 to -0,99 in the range of 10 kHz to 4 MHz. This dependence between frequency and resistance was characterized for all the devices submitted in vacuum, being considered an universal law that governs devices fabricated with disordered material as PS [29].

In the curves obtained of resistance versus frequency of the devices submitted to influence of atmospheres saturated with polar molecules (that is to say, acetone and ethyl alcohol or ethanol), the same exponential relationship described in the expression (1) is observed, however the value of the exponent "s" in this case varied from -0,37 to -0,58.

The non-linearity behaviour between the frequency and the conductivity of devices is accentuated in adsorption process corresponding to the experiments accomplished with saturated atmosphere of acetone. In these processes, "s" varied from -0,37 to -0,52, depending on the characterised device. Comparatively, the value of "s" went equal from -0,47 to -0,58 for the test in ethanol. As already mentioned, the linearity between the electric resistance and the frequency is re-established after the desorption of gaseous substances in the devices, being the results very close of measured conductivity obtained before each test. It is possible to point out that the PS layer neither reacts chemically with the molecules, nor reacts with any residue of the electrolyte, that could be trapped in its pores.

One interpretation of 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 trough a high disordered network of PS, among localised sites, whose transition rate depends both on the spatial distance and on the energy difference between two involved sites. It is assumed that polar molecules, as adsorbed by PS, might lower energy barriers between sites or particles, thus enhancing conductivity.

One of the factors of long response time (around 2000 - 3000 s) of the devices is attributed to the thickness of the
active layer of PS, higher than a few micrometers, necessary because of the poor insulating properties of PS, and needs to be optimised.

About the geometries, it is noted qualitatively that the device with more perimeter (D2 with 16000 µm) has more sensitivity than D11, both with the same geometric area, because the reactions (adsorption and desorption) are happening on the devices periphery.

In sum, it was verified that electrical properties of PS devices change reversibly as submitted in organic vapour atmospheres and can be used to identify them.

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References


