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Physical and chemical characterization of PANI/SiO_2/MPS heterostructure to be used as high sensitivity chemosensor for naphthalene

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ABSTRACT

Macroporous silicon layer was passivated by chemical oxidation and then polyaniline was deposited chemically within the porous structure in order to fabricate a heterostructure to be used as chemical sensor. The structural characterization of this device by scanning electron microscopy reveals the effectiveness of the chemical method for polyaniline deposition in oxidized porous matrix. The analysis by AT-FTIR and Raman spectroscopy shows that polyaniline was deposited in its emeraldine state, which is the most conductive phase, forming a well-defined replica of the porous structure. However, according to the EDS analysis, this polymer layer is non-homogeneous in depth. This feature was also confirmed by electrical measurements of current-voltage and electrochemical impedance at different points between the polymer surface and silicon substrate. In spite of this fact, the immersion of this structure in an ethanolic solution containing low amounts of naphthalene shown that this structure is excellent to be used as chemical sensor for the detection of low concentrations of naphthalene in the order of 30 ppb.

1. Introduction

Porous silicon (PS) is a widely-investigated material because of its singular physical and chemical properties that make this material suitable for different applications such as microstructures [1], light emitting diodes [2], templates for tubes formation [3,4], and so on. Among the different possible applications of PS, one of the most promising material is in the sensor field because of its porous structure provides a high effective surface area as larger than 900 m^2/cm^3 in which a larger number of sensing species can be attached [5,6]. For sensor applications, the chemical reaction between the porous matrix and the target species (analytes) must be avoided because it can damage the porous matrix degrading the sensing effect and promoting non-reproducible responses. For sensors, it is desirable that both optical and electrical responses be only due to the presence of the analyte and not due to the transducer degradation. In this sense, different strategies have been employed to avoid the PS/analyte reaction and the most common of them are the passivation of the porous matrix by silicon oxide growth (SiO_2), carbonation and so on [7,8]. The features of SiO_2 yielded upon crystalline and porous structure were extensively studied by means of different techniques such as Fourier transform infrared (FTIR) and electrochemical impedance spectroscopy (EIS) because of its importance in microelectronics and photonics [8–11]. It was experimentally found that the performance of sensors, made from PS, depends not only on the adequate passivation of the porous matrix, but also upon the suitable functionalization of its surface because this last procedure improves the selectivity and sensitivity of these devices [12,13]. In this sense, many chemical and bio-molecules had been used to functionalize the PS substrate and one of them is polyaniline molecules. The actual state-of-art of chemo- and biosensors devices based in the polyaniline (PANI) molecules pointed that this material is as an excellent candidate not only for passivating, but also to functionalize the transducer devices based in PS structures because of its high stability even under room conditions [14,15]. PANI is a polymer that belongs to the group of synthetic metals because of their electrical properties are like those observed in metals [16], reason for which it was successfully employed in the PANI/PS heterostructure fabrication [17,18]. In these fabrication process, PANI can be introduced into the porous structure by different methods, such as the spin coating, cyclic voltammetry, chemical deposition and so on [16–19]. Thus, the combination of PANI and PS properties would allow the production of sensors with higher stability and larger sensitivity for organic analytes [17,19], such as those reported for detecting diverse kind of gases [14,20]. In addition, the functionalized PANI surface improves its selectivity and sensitivity for detecting heavy metals [21]. The PANI shown to have the ability to detect many chemical compounds [14,15],

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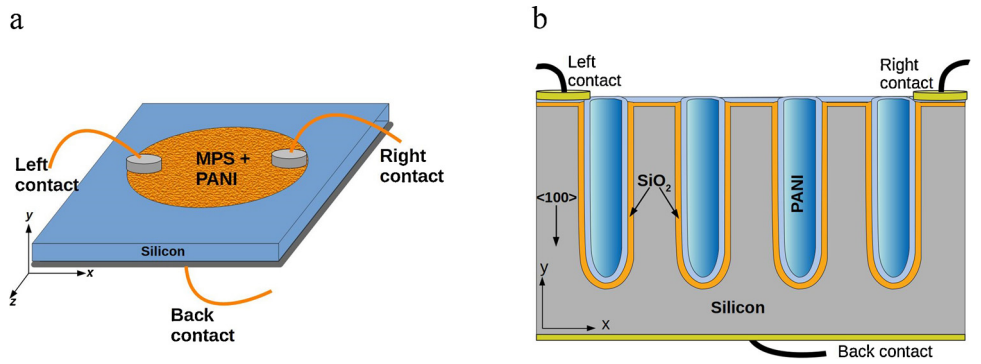

Fig. 1. Schematic representation of (a) top-view, and (b) cross-section of PANI/SiO_2/MPS. heterostructure device showing the contacts for the electrical characterization.

some of them are dangerous for humans and animals. For instance, naphthalene was the first registered pesticide and it is currently used in insecticides and repellents. However, this compound may be hazardous for humans because when it enters the human body it reacts with the cells and can damage tissues [22]. In fact, in recent investigations, it was classified as a possible cause of human cancer [23], proving thus the dangerousness of this compound. The main sources of this pollutant are the emissions from chemical reactions, metal industries and so on, and it can be found in soil and water as contaminant [22,23]. In order to control and quantify the concentration of chemical contaminants in nature it is necessary to find new materials and methods to be used as specific chemosensor with high sensitivity, and one route for this aim is to join the sensitivity of PANI with the larger specific surface area of PS [19,24]. In this sense, here we report the fabrication and characterization of a heterostructure based on the deposition of PANI into the oxidized porous silicon. For this goal, the porous layer was electrochemically oxidized and then PANI was deposited chemically; after, the device was immersed in solutions containing naphthalene as contaminant.

2. Experimental procedure

2.1. Macroporous silicon formation and its passivation

The macroporous silicon structures were fabricated through the following procedure, first the several p-type crystalline Si (100) substrates with $\rho \approx 10\ \Omega$.cm were cleaned following the standard CMOS procedure [25]; after, the backside of them was metalized by 0.5 mm of Al and then they were sintered at 500 °C in N_2 environment in order to obtain a good ohmic contact. For pore formation, the samples were immersed into a solution composed by hydrofluoric acid mixed with dimethylformamide (1:9), placing the samples onto a copper plate embedded into an electrochemical cell made of Teflon and using a platinum sheet with 4.0 cm^2 of area as counter electrode, and then 10 mA/cm^2 of current density was applied by an AUTOLAB potentiometer for 5.0 min. This etching time was controlled by NOVA 1.10 software which is used as interface in this equipment. In the next step, the as-etched MPS was passivated by electrochemical oxidation immersing the sample into H_2SO_4:H_2O (1:5) and then applying 10 mA/cm^2 of current density during 20 min. at the galvanostatic mode. Finally, PANI was deposited in some oxidized MPS samples (OMPS) using the chemical deposition route by immersing the samples in solution composed by 1 M HCl, 1 M aniline and 0.25 M of ammonium persulfate ($(HN_4)_2S_2O_8$) during 24 h in darkness and at room temperature. All aqueous solutions were prepared using distilled water.

2.2. Characterization

The structural characterization of the as-etched MPS, OMPS, and PANI/SiO_2/MPS was carried out with a FEI Nova Nano-SEM 400 scanning electron microscopy (SEM) using the secondary electron detector (TLD-SE). The thickness of the porous layer was measured from the cross-section SEM image and ellipsometry measurement impinging laser beam of $\lambda = 638$ nm, whereas the pores size and frequency of them was quantified with the help of the GRANUL code [26] using for this task the top-view SEM image with area corresponding to 50 μm × 46 μm (3000 X). These results were used to estimate the porosity and effective refractive index of the MPS layer. The electrochemical features of the porous structures were investigated by means of EIS by immersing the porous electrodes (MPS, OMPS and PANI/SiO_2/MPS) in solution of 1 M KCl diluted in ethanol in order to avoid the electrodes oxidation during the experience. For this aim, the experiment was carried out using a three electrodes configuration in which the working electrode was the porous matrix, while a platinum foil with 4.0 cm^2 was employed as counter-electrode and Ag/AgCl electrode as reference. All electrochemical experiments were carried out with the help of an AUTOLAB potentiostat equipment controlled by a NOVA 1.10 software. This equipment was also used to characterize the electrical properties of the PANI/SiO_2/MPS heterostructure by measuring the current-voltage curves and impedance response along the x-axis (from left to right contacts in Fig. 1) as well as along the y-axis between the left side contact onto the PANI surface and the substrate (BC-LC). In addition, to investigate the homogeneity of the electrical properties along the whole porous matrix, a second aleatory point upon the right side of the PANI surface was chosen and then the electrical behavior was recorded between this point and the substrate (BC-RC). The average value of these measurements was made joining the three electrodes (BC-LC-RC). For these measurements, the contacts were made by depositing two silver spots with about 5 mm of diameter onto the PANI surface within the porous region, while the Al layer prior deposited was employed as backside substrate contact. The schematic representation of these contacts is shown schematically in Fig. 1.

The chemical features of PANI within the porous structure were investigated by means of attenuated total reflectance infrared spectroscopy (ATR-FTIR) Spectrum 100 Perkin Elmer equipment and the Raman spectroscopy. For Raman measurements, the samples were excited with a green laser beam ($\lambda = 530$ nm) through 50 times magnification objective that also collects the Raman signal. The in-depth chemical composition of both SiO_2 and PANI within the pores was studied by the Energy dispersion X-ray spectroscopy (EDS), focusing an electron beam spot of about 1 mm. The experience was carried out into an EVO MA15 SEM device.

Finally, in order to evaluate the usefulness of the PANI/SiO_2/MPS heterostructure as chemosensor, this device was immersed into a solution composed by 1 M KCl and ethanol where low amounts of naphthalene ($C_{10}H_8$) was added, in the order of ppb. The sensing effect of this device was studied by measurement of the impedance changes as function of the naphthalene concentration which was measured in the