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A capacitive chemical sensor based on porous silicon for detection of polar and non-polar organic solvents

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ABSTRACT

A capacitive sensor based on porous silicon (PSi) for detection of various polar (ethanol, methanol, acetone, acetonitrile, chloroform) and non-polar organic solvents (*n*-hexane, toluene) was described. The meso-PSi layer with an average pore size of 30 nm was prepared by a galvanostatic electrochemical etching of crystalline silicon in HF-based solution. Surface passivation was conducted by anodic oxidation process and the electrical contacts were made exclusively onto the front porous structure. The as-fabricated sensor exhibits highly sensitive and reversible response toward polar organic molecules during the real-time measurements of capacitance, whereas the capacitive sensing behavior was irreversible and opposite in direction in case of non-polar solvents. The response time was in the order of acetone < methanol < acetonitrile < ethanol < chloroform. The observed response could be understood as the impact of charge redistribution on the pore walls upon organic infiltration, along with changes in the dielectric constant of the porous layer. A comparative study of such different responses is provided. Excellent repeatability of the device was obtained after twelve cyclic tests of acetone, demonstrating stability of the sensor. Long-term stability for the sensor was also observed after four weeks storage. The present approach is useful for the development of a simple, cost-effective sensor for detection of various chemical analytes.

1. Introduction

Sensors are widely used in various technological applications and have become basic enabling technologies in many fields including safety-related areas, diagnostic and drug discovery, environmental monitoring and food industry [1]. Great efforts have been directed toward developing various sensing materials for detection of organic molecules. Particularly, there is increased interest in using porous silicon (PSi) layers in sensing based-devices. PSi that is often produced by an electrochemical etching procedure [2–4] is a promising candidate due to ease of fabrication, large surface area [5], various accessible pore sizes and morphologies [6,7] and controllable surface modification and reactivity [8–13]. Another advantage of PSi is the compatibility with existing silicon processing technology. The dramatic changes in optical or electrical properties of PSi upon adsorption of target molecules have been principally used as key sensing parameters. The optical measurements of PSi have been extensively used in sensing applications, likely due to faster response time, safer to implement than those employing electrical measurements, especially when dealing with flammable gases, vapors, or explosive atmosphere. For example, various PSi structures, including rugate filters [14], Bragg mirrors [15], Fabry-Perot films [16], and micro-cavities [17] have been employed successfully in many chemical and biological sensing applications. In our previous works, we have fabricated 1-D photonic crystal based on PSi rugate filters for optically sensing different types of organic vapors [14,18]. However, the experimental set-up for optical measurements is

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rather complicated with low device sensitivity. Thus, measuring the electrical properties would be an efficient alternative for enhanced sensitivity and a relatively lower-cost operation.

The surface of freshly prepared PSi is often composed of Si hydrides [19,20], which is not appropriate for repeatedly flushed with sensing analytes. Therefore, it is required to stabilize the surface for a proper operation and to prevent uncontrolled oxidation produced by ambient conditions. Oxidation is one of the commonly used and efficient stabilizing approaches. It generates a hydrophilic character to the surface, allowing the sensing of hydrophilic molecules that are miscible with water. Various oxidation techniques to improve the mechanical and chemical stability of PSi have been investigated [21,22]. Thermal oxidation of PSi multilayers [23] is widely used to produce stable filters, however the porous skeleton was found to collapse in some cases [24]. In the present study, the electrochemical oxidation is employed, which has the advantage of easy to implement using the same electrochemical cell used for PSi layer synthesis.

At present, various reports on PSi chemical sensors dealing with its electrical properties are available [25–29]. Electrical sensing of organic chemical solutions together with biomolecules using a thermally oxidized macro-PSi sensor has been investigated [28]. In another report, the observed change in conductance upon exposure to different organic solvents using (~1 μm pore diameter, 20 μm pore thickness) of PSi layers with backside electrical contacts has been extensively studied [26]. Their obtained results revealed a reversible response; however the sensor sensitivity was low with no investigation done on sensor aging and durability. Based on the different approaches adopted by researchers on the electrical sensing using PSi, the capacitive sensing pathway has not been studied in detail. In this work, a capacitive chemical sensor based on electrochemically fabricated meso-PSi layers is employed to detect various polar and non-polar organic solvents. In the present approach the electrical contacts were made exclusively on the front porous surface. From the comparative point of view, the dependence of sensor response on the polar nature of organic molecules is provided. The underlying concept of our approach is based on that, the change in electrical properties upon infiltration of target analytes into the porous layer would enable the detection of organic molecules by recording the magnitude and time evolution of the capacitance shift. The current sensor would contribute to safety control and environmental protection especially in chemical and petrochemical industries that frequently used organic molecules. Results of PSi sensor fabrication and characterization and its performance evaluation are presented and thoroughly discussed.

2. Experimental

2.1. Sample preparation

Mesoporous silicon (PSi) layers were fabricated, according to our previous procedures [30,31], by a galvanostatic electrochemical etching of heavily doped *p*-type Si (1 0 0) wafer with a resistivity of 0.01–0.02 Ω cm; doping density: 7×10^{18} cm^{-3}. The wafer was cut to small pieces with diameters 1.3 cm × 1.3 cm. Each piece was washed by deionized water and sonicated in acetone for 15 min, followed by dipping in 5 wt% aq. HF to remove the native oxides. The electrochemical etching was performed in a cell made of Teflon using a two-electrode set up with a Pt rod served as a counter electrode. The exposed surface area of the Si was 0.78 cm^2, adjusted using an O-ring at the bottom of the cell. A copper plate was used behind the silicon electrode as a current collector. The anodizing solution composed of 28 wt.% $HF/H_2O/EtOH$ with applied current density of 50 mA/cm^2 for anodization time of 75 s.

2.2. Electrochemical oxidation and sample characterization

Surface passivation for as-prepared PSi was performed by anodic oxidation in 1 M H_2SO_4 electrolyte under galvanostatic condition of 5 mA/cm^2 for 20 min. The oxidation of PSi surface is required for stable and proper operation of the device. After the electrochemical oxidation, the porous layers are rinsed in deionized water and ethanol and left for drying naturally. The electrical contacts are made exclusively on the front porous surface by colloidal Ag paint and Cu wires followed by baking at a temperature of 120 °C for 2 h. Field emission-scanning electron microscopy, FE-SEM (JSM-7600F-JEOL), was used to observe the pore size variation in the direction of pore propagation and to determine the thickness of the porous film. Fourier transform infrared (FTIR) spectra were recorded in dried air environment by means of a spectrometer (100 Perkin Elmer-FTIR) for both freshly prepared and oxidized PSi samples. A silicon wafer was used as a reference. The data were averaged over 64 scans with a resolution of 4 cm^{-1}.

2.3. Sensing of organic solvents

To evaluate the sensor response to organic solvents, the device was exposed to various polar molecules, including ethanol, methanol, acetone, acetonitrile and chloroform and to non-polar molecules, typically *n*-hexane and toluene. Individual experiments were performed on different porous layers by adding 10 μl of solvent. Real-time capacitance of the sensor upon exposure to various organic solvents at room temperature were consequently recorded with the electrochemical workstation, ZahnerZennium, Germany, at applied frequency of 100 kHz, a dc bias of 0 V and an ac signal of 100 mV. The impedance as a function of frequency was initially examined for the dry sensor in a frequency range of 100 mHz to 100 kHz. The measurements parameters and the data acquisition and storage were controlled with Thales software.

3. Results and discussions

3.1. Fabrication and characterization of meso-porous silicon

In the formation of PSi by electrochemistry, part of crystalline silicon is principally etched away by the effect of applied current in presence of HF-based solution. The resulting porous layer consists of low-dimensional silicon crystallites with a large distribution of pores. Fig. 1 shows FE-SEM images of top-view (image a) and cross-sectional view (b: inset micrograph) of the porous layer fabricated under the above conditions. The schematic cross-sectional view of the sensor is also depicted in Fig. 1(c). High pore density with an average pore size of 30 nm and a 4.5 μm layer thickness could be recognized. The gravimetric analysis of this sample resulted in 48% porosity. The pores nucleate and propagate along the ⟨1 0 0⟩ direction with no additional side pores. The pores are clearly separated with a small pore-to-pore distance. Such small pore sizes with expected large surface area of meso-PSi play a decisive role in terms of adsorption and infiltration capability during the sensing process [32].

For a proper device operation, a thin layer of surface oxide is usually required. The PSi layer was thus electrochemically oxidized in H_2SO_4 solution at 5 mA/cm^2 for 20 min. The potential transient during oxidation exhibits the same behavior as in case of PSi multilayers for our earlier work [18]. At the initial stage, constant potential is observed, followed by a slight increase in potential with increasing oxidation time. Principally, the concentration of holes on the silicon surface controls the oxidation reaction. The oxidation event initially proceeds from the pore tip as the holes are preferentially available there. Once the pore tip is covered by an oxide layer, feedback control in the galvanostat led to an increase in the applied

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