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Covalent grafting of ion-exchanging groups on porous silicon for microsystem applications

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Abstract

We report the chemical functionalization of porous silicon (PS) by trimethylammoniumpropyl bromide (–$(CH_2)_3N(CH_3)_3{}^+Br^-$) and alkylsulfonic acid (–$C_xH_{2x}SO_3H$) groups for microsystem components. PS was prepared by electrochemical etching of a p-type silicon wafer. Samples of PS were first thermally oxidized at 300 °C and densified at 500 or 700 °C under an inert atmosphere. Mercaptopropyl and trimethylammoniumpropyl bromide groups were grafted on the PS surface via a silanization procedure. The oxidation of mercapto groups was used for the synthesis of –$C_xH_{2x}SO_3H$ groups. The samples were studied by Fourier transform infrared spectroscopy (FT-IR) and temperature-programmed desorption mass spectrometry (TPD-MS). The grafting of –$C_xH_{2x}SO_3H$ groups was found to be dependent on the densification treatment of the oxide layer formed at the surface of PS crystallites by low temperature oxidation. For PS samples thermally oxidized at 300 °C, –$C_xH_{2x}SO_3H$ were not grafted, whereas for PS samples oxidized and densified at 500 or 700 °C, they were successfully grafted. In opposite, the densification treatment of PS samples has no significant influence on the grafting of –$(CH_2)_3N(CH_3)_3{}^+Br^-$ groups.

Keywords: Porous silicon; Sulfonic acid; Quaternary ammonium salt; Ion-exchanging groups; Silanization; Surface functionalization

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1. Introduction

Over recent years there has been many research works on porous silicon (PS) for optical devices, chemical and biological sensors [1,2], micro-arrays [3], micro-reactors [4,5], DNA chips [6] or fuel cells [7]. In fact, porous silicon is compatible with silicon-based technologies and exhibits many attractive properties such as its large surface area (up to 600 m^2/cm^3) and adjustable nanostructure parameters: porosity up to 90% and pore size between 1 nm and 1 μm.

Chemical functionalization of the enormous internal surface of porous silicon with organic fragments found various attractive microsystems applications. Two main approaches are usually used for porous silicon chemical modification: (i) hydrosilylation, which consists in the reaction of alkenes with silane groups (SiH_x with $x=1$, 2 or 3) of as-prepared porous silicon under photochemical or thermal activation [8] and (ii) mild oxidation of porous silicon which results in the formation of a hydroxylated SiO_2 layer ready for the silane chemistry modification commonly applied onto the silica-gel surface [9]. Silica gels with grafted ion-exchanging groups were successfully applied for ion-chromatography [10–12], heterogeneous catalysis [13], solid electrolytes [14], and electrochemical sensors [15,16]. To our knowledge, grafting of alkylsulfonic acid and quaternary ammonium salt groups on the surface of the porous silicon was never described in the literature, and should be very interesting for the fabrication of on chip ion-chromatography devices, solid electrolytic membranes and all other above-mentioned applications. In this paper, we demonstrate how these interesting functions can be achieved in microcomponents based on oxidized porous silicon layers easily fabricated using standard clean room processing steps.

2. Experimental

2.1. Porous silicon fabrication and oxidation

Porous silicon was prepared by anodic etching of p^+-doped ($\rho = 10\ m\Omega\ cm$) double sides polished silicon (100) wafers.

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Anodization was achieved in a Teflon® cell with a copper electrode as backside contact. The counter electrode was made of gold. A constant streaming was applied in order to evacuate hydrogen bubbles formed by the anodization process. Samples were etched in an HF (49%) and ethanol mixture (1:1 by volume) with a 150 mA cm^{-2} anodic current density. Etch stops have been introduced during anodization in order to replenish the solution inside the pores and thus avoiding a vertical porosity gradient in the layer. Samples of 50 μm thickness and 65% porosity were detached from the bulk silicon by switching to the electropolishing regime at the end of the anodization process (pulse at 1 A cm^{-2} during 5 s) for characterization by transmission FT-IR. Porous silicon morphology was controlled by gravimetric measurements for porosity and Raman spectroscopy for crystallite size and in-depth homogeneity.

Samples referred as PS1 were oxidized at 300 °C during 1 h in dry oxygen. The same procedure, followed by a densification step [17] of the oxide layer formed at the surface of silicon nanocrystallites for 1 h in dry nitrogen at 500 and 700 °C, was performed to prepare the samples referred as PS2 and PS3, respectively.

2.2. Characterization methods

Transmittance FT-IR spectra of PS samples were recorded in ambient conditions and also after the drying of the samples at 120 °C under vacuum. A laboratory-made cell allowing the sample transfer from the heated section to the detection section equipped with CaF_2 windows was used for this purpose. During TPD-MS measurements, samples of PS were heated under high vacuum (pressure < 10^{-3} Pa, heating rate = 0.167 K s^{-1}). Then, volatile products of decomposition were analyzed by mass-spectrometry (MS) [18]. Gas ionization was done by electronic impact at −70 eV and mass fragments between 2 and 200 atomic mass units (amu) were recorded.

2.3. Chemical modifications of porous silicon

Procedures of *N*-trimethoxysilylpropyl-*N*,*N*,*N*-trimethylammonium iodide (TMA^+I^-) synthesis and silanization reactions were carried out using anhydrous organic solvents under an argon inert atmosphere via Shlenk technique. Just before the silanization, oxidized PS layers were dried at 120 °C for water desorption.

2.3.1. Synthesis of N-trimethoxysilylpropyl-N,N,N-trimethylammonium iodide

TMA^+I^- was synthesized by the Hoffman reaction in Scheme 1.

0.01 mole of 3-aminopropyltrimethoxysilane was mixed with 0.04 mole of methyl iodide in 50 ml of methanol during 1 h. Then, 0.02 mole of sodium metoxide in 10 ml of methanol was added dropwise to the reaction mixture, which was stirred for 20 h. Afterwards the solvent was evaporated under vacuum. ^1H NMR spectrum, recorded in $CDCl_3$ solution of the resulted solid mixture (TMA^+I^- and NaI), presented four peaks at 0.4 t(2H), 1.65–1.8 m(2H), 3.1–3.3 m(11H), 3.51 s(9H) ppm, that showed the formation of TMA^+I^-. Bands of CH_x stretching (3014, 2962, 2930, 2855 cm^{-1}) and bending (1490, 1482, 1421 cm^{-1}) and also bands of Si–O vibrations (1098, 1025, 800 cm^{-1}) in the FT-IR spectrum confirmed the synthesis of TMA^+I^-.

2.3.2. Chemical modification of PS by anion-exchanging groups

In order to graft anion-exchanging groups, oxidized PS samples were treated with 15% of TMA^+I^- and NaI mixture dissolved in acetonitrile for 15 h under reflux. Then, the samples were washed several times by boiling acetonitrile, dried and washed with saturated KBr aqueous solution in order to exchange iodide to bromide anion. Finally, PS-TMA^+Br^- samples were washed with deionized water, ethanol and dried in air at 120 °C.

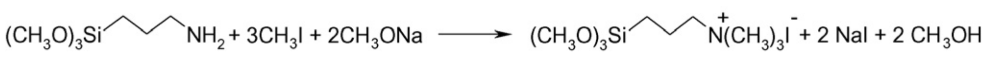
2.3.3. Chemical modification of PS by cation-exchanging groups

To graft mercaptopropyl groups ($–C_3H_6–SH$) on the surface of PS crystallites, oxidized PS samples were dipped in toluene solution containing 1% of pyridine and 15% of 3-mercaptopropyltrimetoxysilane at 60 °C for 20 h. Then the samples were washed with toluene at 60 °C and dried in air at 120 °C. The oxidation of mercapto groups (–SH) to get the sulfonic acid ($–SO_3H$) groups was realized in a 30% H_2O_2 solution at 35 °C for 1 h, similarly as it has been done for silica modifications [10–19]. PS samples with grafted $–SO_3H$ groups were washed with water from the excess of reactants, then with a 3.5% hydrochloric acid solution and finally with deionized water and absolute ethanol.

3. Results and discussion

3.1. FT-IR characterization of PS layers after oxidation and densification

The chemical composition of the surface of initial (PS0) and oxidized (PS1) PS layers was analyzed by FT-IR (Fig. 1). In the spectrum of the unmodified PS0 sample, only the vibration modes of SiH_x groups which are typical for PS samples [20] were observed: stretching modes $\nu_s(SiH_2)$ at 2137 cm^{-1}, $\nu(SiH)$ at 2114 cm^{-1}, $\nu_{as}(SiH_2)$ at 2088 cm^{-1}, scissor modes $\delta(SiH_2)$ at 906 cm^{-1}, and wagging modes $\omega(SiH_2)$ at 660 cm^{-1}, $\omega(SiH)$ at 625 cm^{-1}. The oxidation at 300 °C (PS1) resulted in the significant decrease of SiH_x modes intensity and the appearance of O_2SiH stretching mode at 2208 cm^{-1} and O_3SiH stretching mode at 2264 cm^{-1}. Intense bands between 1200 and



Scheme 1.