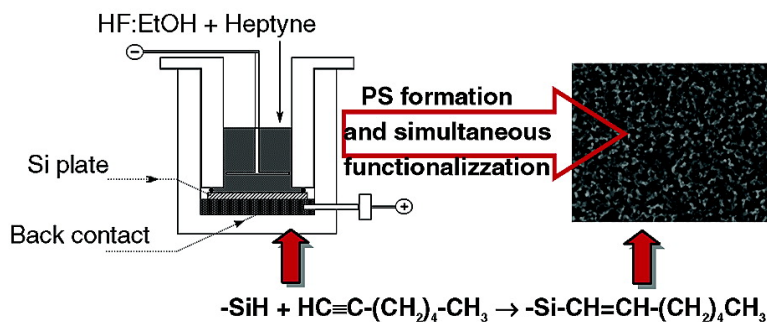


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In Situ Functionalization of Porous Silicon during the Electrochemical Formation Process in Ethanoic Hydrofluoric Acid Solution

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The surface chemistry of silicon is of general importance in fundamental studies and of crucial interest in modern technology. In the case of porous silicon (PS), the possibility to modify the surface properties through the chemisorption of organic molecules (functionalization)^{1,2} is of great relevance for applications in various fields: optoelectronics, sensors, biosensors, and photovoltaics. Until now, several methods have been shown to be useful for the preparation of organic monolayers covalently attached through Si–C and Si–O–C bonds to PS surfaces under photochemical,^{3–6} electrochemical,^{7–9} and thermal^{10–12} conditions as well as using a catalyst.^{13–15} All these methods, employed after the PS preparation, require some experimental procedures to avoid the contamination and oxidation that are always in competition with the functionalization process.

In this Communication, a new method for the in situ preparation–functionalization of PS layers is described. It is shown that this method is simple, fast, and quite efficient. The basic idea is that of dissolving the HF-compatible organic molecules of interest directly inside the HF ethanoic solution to be used for the electrochemical preparation of the PS layers. During the partial anodic dissolution of silicon to form the PS layer, the presence of the organic molecules at the Si sites where the Si–H bonds are attacked and Si atoms are dissolved can allow an efficient interaction with the Si atoms to form the Si–C bonds and hence to realize the functionalization reaction in optimal conditions. The oxidation is limited by the presence of HF that normally leaves an oxide-deprived Si surface covered by Si–H bonds. The duration of the process is that of the normal formation of the PS layer, of the order of seconds or minutes. In this case, the functionalization occurs together with the PS formation in a single-step process (in situ functionalization), without the necessity of subsequent and longer procedures in controlled environments (e.g., vacuum treatments, drybox, etc.). Finally, this method has a unique and very appealing feature, namely the possibility to confine the adsorbed species in selected layers in a PS stack (or multilayer PS system), i.e., only in those prepared in the presence of the organic molecules.

To prove these ideas, a series of samples has been prepared and investigated by FTIR. The selected organic molecules were fluoridic acid resistant and mainly with a triple terminal bond, although molecules with internal triple bonds and with different conjugated double bonds have been also studied. The results concerning the functionalization of PS with 1-heptyne (C₇H₁₂) molecules are here reported and discussed in detail.

The samples were prepared by the partial anodic dissolution of p⁺ Si (100) wafers with resistivity of 0.01 Ω cm in an electrochemical cell containing an HF (50%)–EtOH solution (1:2 by volume) and a certain concentration of 1-heptyne molecules. For

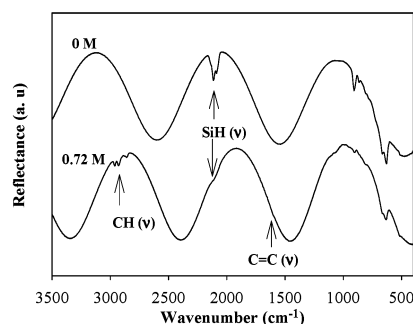


Figure 1. FTIR reflection spectra of a PS film prepared without 1-heptyne (0 M) and with 1-heptyne (0.7 M). The arrows indicate the frequencies of the Si–H_x bands and of the main 1-heptyne bands.

the experiments, a set of mesoporous PS films was prepared with the same current density and etching time (60 mA/cm², 100 s) and different concentrations of heptyne, from 0 to 0.9 M (close to the saturation value). After the preparation–functionalization procedure, the samples were washed in water, ethanol, and acetone. The IR reflection spectra, measured after each washing, were recorded in the range 400–5000 cm^{–1} with a resolution of 4 cm^{–1} using a BioRad FTIR-40A Fourier transform infrared spectrometer; the angle of incidence was fixed at 20°. To obtain more quantitative data, all the measured spectra have been subjected to data reduction and compared with model spectra obtained by suitable calculations.¹⁶ Through this analysis, the porosity, the thickness, and the absorption coefficient α for the main absorption bands present in the reflection spectra were obtained.

The IR reflection spectra of two PS samples, prepared without (0 M) and with (0.7 M) 1-heptyne, measured after washing with water are shown in Figure 1. In the spectra, modulated by the interference fringes, the most important bands are indicated by arrows. Subsequent washing treatments, even with polar solvents, do not modify the infrared spectra, thus indicating that stable surface species were formed on the PS surface.

The comparison of the two spectra in Figure 1 indicates that the presence of 1-heptyne in the solution modifies only slightly the structure (i.e., the thickness and the porosity) of the PS layer, the two interference patterns being almost equal. Moreover, the spectrum of the sample prepared in the presence of the organic molecules reveals the presence of clear features attributable to Si-bonded 1-heptyne species. Indeed: (i) The absence of the terminal $\nu_{\text{C–H}}$ at 3300 cm^{–1} excludes physisorbed heptyne. (ii) All the other bands due to the C–H vibrations, stretching as well as bending, are recognizable (2960, 2928, 2876, and 2860 cm^{–1} $\nu_{\text{C–H}}$; 1464 cm^{–1} δ_{CH_2} ; 1376 cm^{–1} δ_{CH_3}). (iii) The $\nu_{\text{C}\equiv\text{C}}$ triple bond stretching (around 2200 cm^{–1}) is totally absent and is replaced by the $\nu_{\text{C=C}}$ double bond stretching (around 1600 cm^{–1}), as is expected for molecules chemisorbed on silicon through the terminal C atom of

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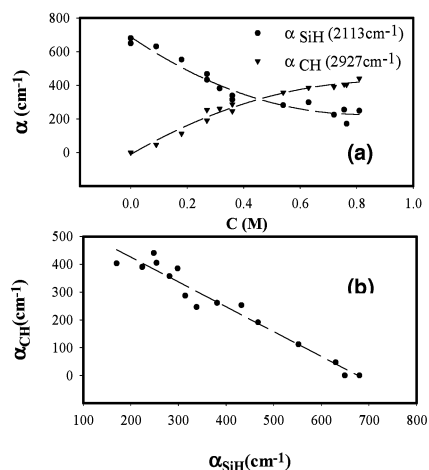
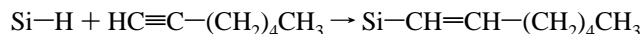


Figure 2. (a) Absorption coefficients α_{CH} , in the C–H region (at 2927 cm^{-1}), and α_{SiH} , in the Si–H region (at 2113 cm^{-1}), as a function of the 1-heptyne concentration, C , in the anodic solution. (b) α_{CH} (2927 cm^{-1}) vs α_{SiH} (2113 cm^{-1}). The dashed lines are a guide to the eye.

the original triple bond, according to the following hydrosilylation² reaction:



(iv) The vinyl =CH stretching slightly above 3000 cm^{-1} , usually very weak or undetectable,^{2,4} could be attributed to a small shoulder² present at 3037 cm^{-1} . (v) Some weak bands, attributable to Si–O vibrations, are present in the 1000–1100 cm^{-1} range with higher intensity than in the unfunctionalized samples. (vi) The strong reduction of the signal due to the SiH species, with little oxidation, is clear evidence that in the functionalized PS layer the chemisorbed species have replaced the hydrogen in a large fraction of the surface sites of the PS surface normally occupied by silicon hydride species.

It is important to stress that if an unfunctionalized PS sample is kept in contact with the same (0.7 M) 1-heptyne HF ethanoic solution, for a time as long as 1000 s, no significant functionalization is achieved. This fact also demonstrates that the presence of the organic molecules in the solution during the electrochemical formation of the PS material is essential for the effectiveness of this functionalization method. Hence, only PS layers formed in the presence of the organic molecules are functionalized. Besides, the integrated intensities of all the 1-heptyne characteristic bands increase with the increase of the 1-heptyne concentration in the anodic solution, whereas the signal of Si–H species decreases. As an example, we can see in Figure 2a the dependence on the 1-heptyne concentration (from 0 to 0.8 M) of the absorption coefficient in the C–H stretching region (at 2927 cm^{-1}) and in the Si–H stretching region (at 2113 cm^{-1}). These results indicate an evident inverse correlation, clearly illustrated in Figure 2b, between the surface abundance of the chemisorbed molecules and that of the silicon hydride species. From the relative decrease of the integrated intensities of the Si–H absorption signal, the average efficiency of the functionalization process can be evaluated.¹⁴ In this case, we found values as high as 50–60%.

To further study the effects induced on the PS material by the presence of the organic molecules in the preparation solution, we

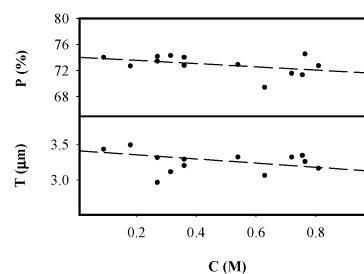


Figure 3. Porosity, P , and thickness, T , of PS samples as a function of the 1-heptyne concentration, C , in the anodic preparation solution.

have also measured the dependence of thickness and porosity on the heptyne concentration. These parameters slowly decrease with the increase of the 1-heptyne concentration, as illustrated in Figure 3, thus indicating that the chemical species interact with the Si atoms on the sample surface and modify slightly the PS morphology. Similar dependencies have been obtained also for samples prepared with different current densities. Finally, the variations of porosity and thickness can be controlled, and the use of “calibration” curves similar to those of Figure 3, measured for various current densities, should allow the design and the preparation of PS layers having the desired morphological properties and amount of functionalization.

In conclusion, we have demonstrated that this functionalization procedure, accompanied by low-level oxidation, is simple, fast, and quite effective. Preliminary results indicate that selective functionalization of single layers in a stack of PS can really be achieved by this method. Further work is in progress.

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Supporting Information Available: Absorption coefficient α for the main absorption bands present in the reflection spectra as a function of the frequency for the same samples as in Figure 1 (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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