

Microwave-Assisted Chemical Functionalization of Hydrogen-Terminated Porous Silicon Surfaces

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This paper describes the chemical functionalization of hydrogen-terminated porous silicon surfaces with simple and functional 1-alkenes under microwave irradiation to give organic monolayers covalently attached to the surface through Si–C bonds. Using microwaves as a source of energy led to a remarkable increase in the rate of the hydrosilylation reaction and a higher surface coverage. This technique yields highly stable organic monolayers and allows the introduction of different functional groups on the surface (acid and ester) required for immobilization of more complex structures on the surface.

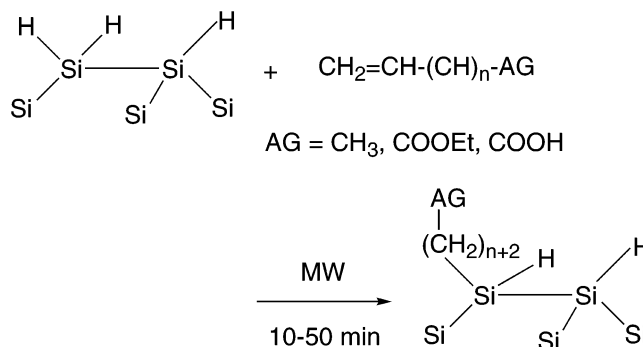
Introduction

Chemical functionalization of semiconductor surfaces has many potential applications ranging from surface passivation and stabilization to development of new strategies for immobilization of either chemical or biological species on the surface and detection of diverse interactions characterizing biological and chemical systems. Silicon-based structures are capital for such applications, because they offer the possibility for using the well-established microfabrication methods for integration of chemical and biological functionality into microelectronics platforms. Moreover, porous silicon (PSi) has the advantage of its high surface area and was found to be photoluminescent and electroluminescent.¹ Potential applications based on electrical and/or optical measurements for sensing chemical and biochemical interactions on the surface have been demonstrated using PSi.^{2,3} More recently, an important step toward utilization of PSi for biomedical applications has been achieved. Canham et al. have shown that PSi layers of low porosity are active in vivo and that hydroxyapatite could be grown on the PSi matrix.^{4–6}

Hydrogen-terminated PSi surfaces prepared by electrochemical dissolution of crystalline silicon in HF-based solutions exhibit very good electronic and optical properties.¹ However, these properties are affected by the chemical transformations occurring upon exposure of these surfaces to ambient air. Slow oxidation of the surface tends to deteriorate the good properties of this material. Several methods including deliberate oxidation under controlled thermal or electrochemical conditions have been elaborated to stabilize the porous matrix.⁷ Recently, much effort has been devoted toward PSi passivation using chemical derivatization of the freshly prepared surfaces by replacing silicon–hydrogen (Si–H_x) bonds with more stable Si–C or Si–O–C bonds, under various conditions.⁸ The organic-modified PSi surfaces have shown a very good stability in different

organic and aqueous buffered solutions. This high improvement in the stability is a real asset for future applications of the resulting hybrid materials (PSi/organic monolayer). We have used a thermal treatment to functionalize the PSi surface with a high coverage.^{9,10} This technique is simple to carry out and tolerates different functional groups (ester and acid functional groups).^{11,12} We have successfully used this approach to stabilize the photoluminescent properties of the PSi surface,¹³ as well as the electroluminescence (EL) efficiency and EL output intensity of a PSi-based diode under continuous operation.¹⁴

This paper describes a method based on microwave (MW) activation for chemical derivatization of PSi surfaces with 1-alkenes. Utilization of microwave irradiation as a source of energy leads to a net acceleration and a remarkable rate enhancement of the hydrosilylation reaction of PSi surfaces with 1-alkenes. This method produces highly stable organic monolayers covalently attached to PSi surfaces and allows the introduction of different functional groups required for immobilization of more complex structures on the PSi surface.



Results and Discussion

Using microwave activation was motivated by the recent reports on the big impact of MW-assisted organic^{15–17} and solid-phase organic¹⁸ reactions in terms of reduction of reaction times, conversion enhancement, and specificity. Moreover, the specific absorption of microwave energy by silicon, as a result of an

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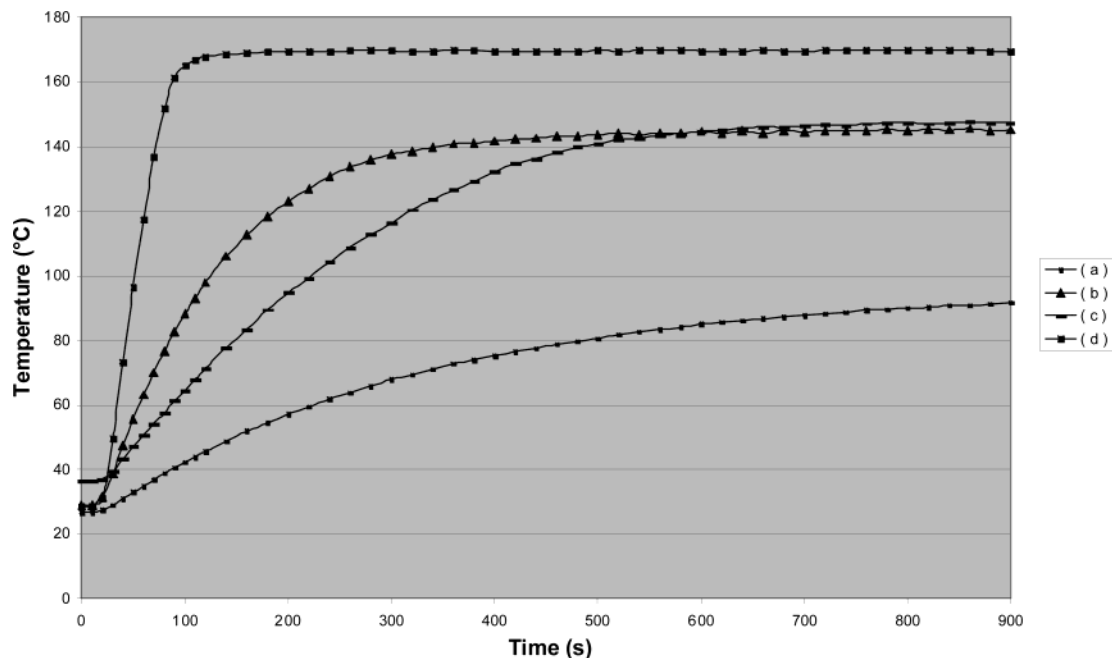


Figure 1. Profiles of temperature rise under microwave irradiation at a restituted fixed emitted power of 300 W: 1-dodecene (a), ethyl undecylenate (b), undecylenic acid (c), and the reaction mixture of 1-dodecene and porous silicon at an optimal temperature programming of 170 °C by modulation of emitted power (d).

intrinsic property, leads to confined heating in the near surface of the material. Selective heating of the substrate was expected to influence the course and the rate of the hydrosilylation reaction rate at the surface. Silicon wafers used in this study have a resistivity of 1–15 ohm cm, which is in the range of a maximum absorption of MW radiation.¹⁹

Prior to carrying out the reactions, we have studied the thermal behavior of the reactants under MW irradiation, which is believed to be dominated by the polarity of the system.^{20,21} In the absence of a silicon wafer in the mixture, the thermal MW effect was not very pronounced in the case of 1-dodecene. This compound is poorly polar and therefore quasi MW transparent. The rise in the temperature was very slow and reaches a plateau at 90 °C after 15 min for a restituted MW power of 300 W, the optimal available from the equipment (Figure 1a). Under the same conditions, the more polar ethyl undecylenate (Figure 1b) and undecylenic acid (Figure 1c) have shown more important rises in temperature, reaching now more rapidly a plateau at 148 °C. When a silicon wafer was introduced in neat 1-dodecene, the mixture shows a very rapid increase in the temperature and reaches 170 °C in less than 2 min (Figure 1d). It is important to notice that this temperature was measured in the liquid phase (by infrared detection or via an optical fiber) because we were not able to evaluate directly the temperature of the silicon substrate.

Hydrogen-terminated PSi surfaces used in this work have been prepared by anodic dissolution of Si(100) (B-doped, p-type) in HF/EtOH = 1/1 (v/v) at a current density of 40 mA/cm². Figure 2a displays the transmission FT-IR of a freshly prepared PSi sample. It exhibits peaks due to stretching modes $\nu_{\text{Si-H}}$ at 2115 cm⁻¹, Si-H₂ scissor mode $\delta_{\text{Si-H}_2}$ at 912 cm⁻¹, and $\delta_{\text{Si-H}}$ at 669 and 629 cm⁻¹. A small peak at 1037 cm⁻¹ (Si-O-Si stretching mode), which is present in all PSi samples, results most likely from a small oxidation of the reactive surface. Reaction of hydrogen-terminated PSi with 1-dodecene at 170 °C for 15 min under MW irradiation led to the formation of an organic monolayer covalently attached to the surface through an Si-C bond. Additional peaks at 2924 cm⁻¹ (C-H stretching modes) and at 1465 cm⁻¹ (methylene bending modes) of the

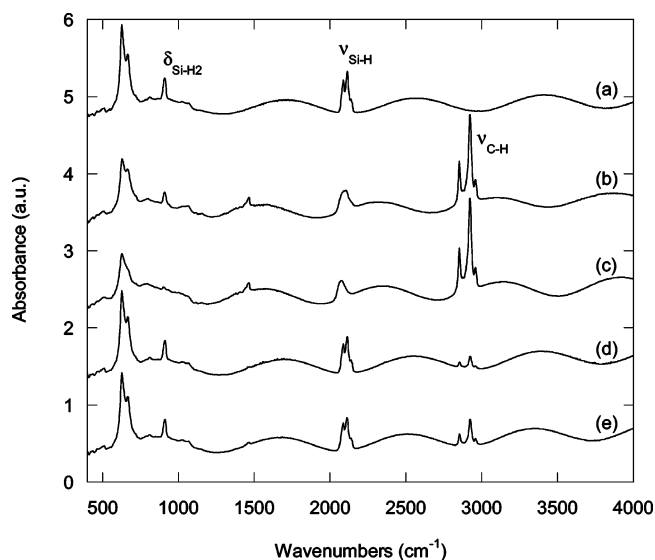


Figure 2. Transmission-mode FTIR spectra of freshly prepared porous silicon before (a), and after chemical functionalization with 1-dodecene under microwave irradiation for 15 min at 170 °C (b) and 30 min at 170 °C (c), and after thermal derivatization with 1-dodecene at 180 °C for 15 min (d) and 30 min (e).

alkyl chain appear (Figure 2b). A large decrease of $\nu_{\text{Si-H}}$ (2115 cm⁻¹), $\delta_{\text{Si-H}_2}$ (912 cm⁻¹), and $\delta_{\text{Si-H}}$ (669 and 629 cm⁻¹) intensity was observed, indicating that the reaction was very efficient and took place with silicon-hydride consumption. Moreover, there was no increase of the $\nu_{\text{Si-O-Si}}$, consistent with a thermal process occurring without any apparent oxidation of the surface. MW irradiation of hydrogen-terminated PSi in 1-dodecene at 170 °C for 30 min gave comparable results (Figure 2c). We have used FTIR spectroscopy to monitor the efficiency²² of the reaction by simple evaluation of the ratio of the integrated area of the Si-H intensity before and after chemical derivatization. The PSi surface modified with 1-dodecene under MW irradiation at 170 °C for 15 min gave an efficiency of 19%. Increasing the MW irradiation time while keeping the

temperature constant at 170 °C led to higher conversion. Figure 2c displays the FTIR spectrum of a PSi surface that has been functionalized with 1-dodecene under MW irradiation for 30 min at 170 °C. It shows features similar to those in Figure 2b, but with a lower Si-H intensity. In fact, the reaction efficiency has doubled (38%). Increasing the temperature to 180 °C for 30 min did not improve the reaction efficiency. An average reaction efficiency of 28% was reported for the reaction of freshly prepared PSi surface with 1-dodecene catalyzed with Lewis acid.²³ To better emphasize the MW effect on the hydrosilylation reaction, we have carried out the reaction in an oil bath at 180 °C. Reaction of freshly prepared PSi surface with 1-dodecene at 180 °C in the same Pyrex vessel under continuous argon bubbling for 15 min (Figure 2d) and 30 min (Figure 2e) led to very little chemical grafting of the dodecyl moieties. This noticeable difference in the reactivity may be associated with a large temperature gradient between the liquid phase and the near surface of the PSi sample. Because the MW irradiation was dominantly absorbed by the PSi sample, a higher temperature may arise at the PSi/1-dodecene interface leading to a better surface coverage. This effect could be considered as purely thermal. However, it is well documented in the literature that an increase in the polarity during the reaction (for example, formation of charged intermediates) would favor MW absorption and therefore will cause an increase in the reaction rate. However, it is hard to draw any conclusion at this stage since the reaction mechanism should concern reaction between two neutral molecules presumably via a polar transition state, and therefore induces a specific nonthermal MW effect by reduction of the energy of activation.¹⁵

To evaluate the chemical stability of the functionalized PSi surfaces, we have subjected the PSi surface modified with 1-dodecene under MW irradiation at 170 °C [surface (c) in Figure 2] to the following sequential treatments: water at RT for 1 h, water at 100 °C for 1 h, 1.2 M HCl aqueous solution for 1 h at 100 °C, and immersion in 2.4 M HCl aqueous solution at 100 °C for 2 h. Moreover, the PSi functionalized surfaces are stable in aqueous HF and KOH solutions at room temperature. The dodecyl-terminated PSi surface was found to be robust and no deterioration was observed after these treatments as evidenced by FT-IR spectroscopy. There are no apparent changes in the IR spectra of both C-H and Si-O-Si stretching regions. This clearly indicates that the remaining Si-H bonds on the surface are well-passivated against oxidation and corrosion.

To generalize this technique, we have tested 1-alkenes bearing end functional groups (ester or acid functional groups). Hydrosilylation reaction of ethyl undecylenate with hydrogen-terminated PSi surface under MW irradiation for 10 min at 180 °C led to chemical attachment of the organic monolayer on the PSi surface. The presence of stretching modes at 1740 cm^{-1} ($\nu_{\text{C=O}}$) and at 1179 cm^{-1} ($\nu_{\text{C-O}}$), characteristic of the ester function, along with the C-H stretching modes at 2924 cm^{-1} , and the absence of C=C stretching mode in the IR spectrum (Figure 3a) are in agreement with the formation of an organic monolayer covalently attached to the PSi surface and bearing an ester end functional group.¹¹ The reaction took place with no or very little oxidation of the surface. The reaction efficiency was found to be comparable to the one obtained with 1-dodecene. When the ester-terminated PSi surface was heated in 2.4 M HCl aqueous solution for 9 h at 100 °C, only the ester hydrolysis was observed as indicated in the IR spectrum (Figure 3b). In fact, there is a disappearance of the peaks at 1740 and 1179 cm^{-1} characteristic of the ester function and appearance of new

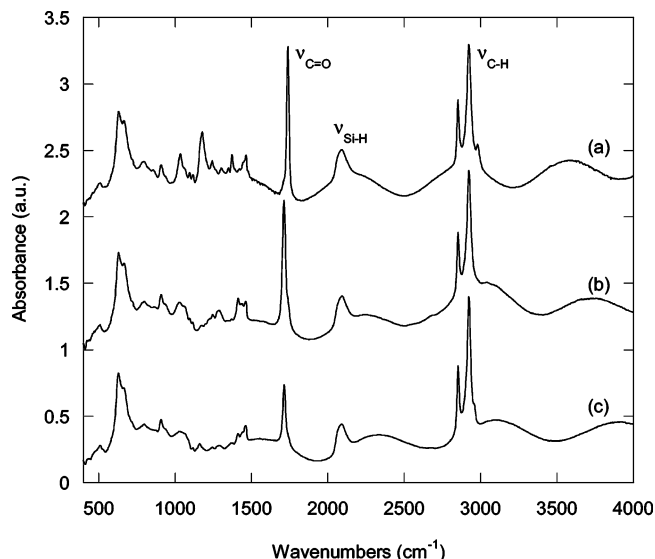


Figure 3. Transmission-mode FTIR spectra of porous silicon surfaces chemically derivatized with ethyl undecylenate under microwave irradiation for 10 min at 180 °C (a), surface (a) treated with 2.4 M HCl at 100 °C for 9 h (b), and porous silicon surface functionalized with a mixture of 1-dodecene/undecylenic acid (1/1) for 50 min at 180 °C.

peaks at 1715 and 3080 cm^{-1} assigned to the stretching modes ($\nu_{\text{C=O}}$) and (ν_{OH}) of the acid, respectively. Again, the MW-assisted chemical functionalization of PSi surfaces is very convenient and efficient to prepare very stable and robust organic monolayers. Finally, we have modified PSi surfaces with a mixture of undecylenic acid and 1-dodecene (v/v = 1/1) at 180 °C for 50 min using MW irradiation. The surface was characterized using transmission FT-IR and displays peaks comparable to the surface (in Figure 3b) obtained by hydrolysis of the ester-terminated PSi surface (Figure 3c). This result is somehow surprising, because the polar OH group borne by the acid function did not compete with the hydrosilylation reaction under MW activation. This result is comparable to the reaction pathway observed when the PSi surface was modified with undecylenic acid under thermal conditions.¹² There is no evidence for Si-O-C formation in the IR spectrum, as a result of the OH attack on the Si-H or Si-Si bonds. The reaction takes place selectively at the carbon-carbon double bond without any apparent oxidation of the surface. However, the reaction with undecylenic acid alone or mixed with 1-dodecene requires longer times (even the reaction conditions were not optimized). This may be due to the slow diffusion of the acid inside the hydrophobic porous layer.

In conclusion, we have successfully used MW irradiation to derivatize hydrogen-terminated PSi surfaces with a high chemical yield and a substantial increase in the reaction rate. We have shown that the chemical process can effectively passivate and protect the PSi surface against corrosion.

Future work will focus on optimization of the reaction conditions and exploration of various organic molecules bearing different functional groups to test the selectivity of the process.

Experimental Section

Materials. All cleaning and etching reagents were clean room grade. All chemicals were reagent grade or higher and were used as received unless otherwise specified. 1-Dodecene, ethyl undecylenate, undecylenic acid, and dichloromethane (CH_2Cl_2) were all available from Aldrich.

Sample Preparation. Double-side polished Si(100) oriented p-type silicon wafers (boron-doped, 1–15 ohm cm resistivity) were first cleaned in 3:1 concentrated H₂SO₄/30% H₂O₂ for 15 min at 80 °C and then rinsed copiously with Milli-Q water. The clean wafers were immersed in 5% aqueous HF solution for 1 min at room temperature to remove the native oxide. The hydrogen-terminated surfaces were electrochemically etched in a 1:1 (v/v) solution of pure ethanol and 48% aqueous HF for 2 min at a current density of 40 mA/cm². After etching, the samples were rinsed with pure ethanol and were dried under a stream of dry nitrogen prior to use.

Microwave experiments were performed in a Synthewave 402 monomode reactor from Prolabo Company²⁴ operating at 2450 MHz. All reactions were conducted in a specially adapted open cylindrical Pyrex vessel containing 1-alkene and the porous silicon sample under a continuous argon bubbling and mechanical stirring to ensure oxygen elimination and temperature homogeneity in the solution. The mixtures were heated into the monomode reactor at temperatures and for given reaction times as indicated in the text. The reactor was cooled to room temperature. The excess of unreacted and physisorbed reagent was removed by rinsing, at room temperature, with dichloromethane and then the sample was dried under a stream of nitrogen.

The temperature was controlled throughout the reaction and evaluated by an infrared detector that indicated the surface temperature (IR detector was calibrated by according to the emissivity factor using an optical fiber inside the reaction mixture). A computer system was used for automatic control of the irradiation (power and temperature) as well as data processing.

FT-IR Spectroscopy. Transmission FT-IR spectra were recorded using a Bomem MB100 spectrometer at 4 cm⁻¹ resolution. The samples were mounted in a purged sample chamber. To avoid significant errors during the efficiency calculation, we placed the sample in the same position before and after chemical modification. Background spectra were obtained using a flat untreated Si(100) wafer that had been dipped in 5% HF aqueous solution to remove the native oxide layer.

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