

Derivatization of Porous Silicon by Grignard Reagents at Room Temperature

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Porous Si is a noteworthy material due to its luminescent properties and promise of compatibility with current semiconductor fabrication schemes based on silicon.¹ Porous Si forms by the anodic dissolution of crystalline silicon in a HF-based electrolyte, and this process produces a hydrogen-terminated Si surface. Several methods for chemically modifying this surface have been reported;^{2–7} however, these derivatization reactions are limited to photo- or electrochemical methods that attach one or two carbon fragments to the surface ($\text{CH}_3\text{-Si}$ and $\text{RCO}_2\text{-Si}$; $\text{R} = \text{H}, \text{CH}_3$) and thermal treatments that attach olefins and alcohols. Grignard reagents have been reported for the functionalization of Si surfaces by Lewis et al.⁸ who developed a two-step procedure where the H-terminated Si surface was first chlorinated radically by PCl_5 and subsequently quenched with a Grignard reagent (80 °C for 30 min to 8 days).⁹ On porous Si, Chazalviel has used electrochemical stimulus to attach methyl groups using CH_3MgBr .⁶ Our experimental results demonstrate the direct formation of covalently attached organic layers on porous Si by Si–C bonds using a variety of Grignard reagents at room temperature without the intervening chlorination step or the need for photo- or electrochemical methods that often proceed with oxidation of the substrate.

Figure 1a shows a diffuse reflectance infrared Fourier transform (DRIFT) spectrum for a porous silicon sample that was formed by the electrochemical etching of Si(100) in HF acid/ethanol. The spectrum exhibits peaks for Si– H_x stretching mode at 2116 cm^{-1} , Si–O stretching mode at 1031 cm^{-1} , and Si– H_2 bending mode at 914 cm^{-1} .^{2–6} After exposure of porous silicon to 1 M decylmagnesium bromide in ether for 2 h at 25 °C and subsequent quench by addition of 1 M HCl in ether, its spectrum (Figure 1b) contains alkyl stretching and bending absorptions between 2850 and 2950 cm^{-1} and 1300 and 1470 cm^{-1} , respectively, for the attached decyl chain. In the Si– H_x stretching region, the absorption for Si– H_3 exhibits the biggest decrease compared to those for Si–H and Si– H_2 suggesting that the Si– H_3 moiety is the most reactive species and is lost during reaction.

To ensure that the hydrocarbon adsorption bands in Figure 1b were not the result of adventitious contamination, we performed additional derivatization reactions using labeled Grignard reagents.

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(1) (a) Lehmann, V. *Materials Lett.* **1996**, *28*, 245–249. (b) Hamilton, B. *Semicond. Sci. Technol.* **1995**, *10*, 1187–1207.

(2) Kim, N. Y.; Laibinis, P. E. *J. Am. Chem. Soc.* **1997**, *119*, 2297–2298.

(3) (a) Lee, E. J.; Ha, J. S.; Sailor, M. J. *J. Am. Chem. Soc.* **1995**, *117*, 8295–8296. (b) Lee, E. J.; Bitner, T. W.; Ha, J. S.; Shane, M. J.; Sailor, M. J. *J. Am. Chem. Soc.* **1996**, *118*, 5375–5382.

(4) Glass, J. A., Jr.; Wovchko, E. A.; Yates, J. T., Jr. *Surf. Sci.* **1995**, *338*, 125–137.

(5) Warntjes, M.; Vieillard, C.; Ozanam, F.; Chazalviel, J.-N. *J. Electrochem. Soc.* **1995**, *142*, 4138–4142.

(6) Chazalviel, J.-N.; Vieillard, C.; Warntjes, M.; Ozanam, F. *Proc. Electrochem. Soc.* **1996**, *95*, 249–257.

(7) Linford, M. R.; Fenter, P.; Eisenberger, P. M.; Chidsey, C. E. D. *J. Am. Chem. Soc.* **1995**, *117*, 3145–3155.

(8) Bansal, A.; Li, X.; Lauermaun, I.; Lewis, N. S.; Yi, S. I.; Weinberg, W. H. *J. Am. Chem. Soc.* **1996**, *118*, 7225–7226.

(9) Hydrogen terminated Si surfaces are easier to manipulate and maintain than chlorinated Si surfaces, as the latter are more sensitive to water.

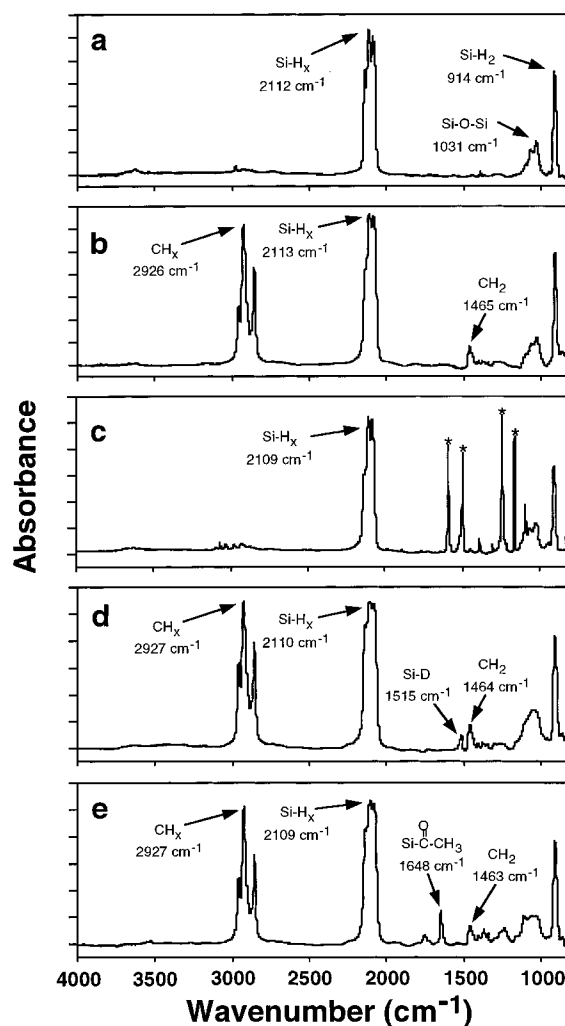


Figure 1. Diffuse reflectance infrared spectra for (a) underivatized porous silicon and porous silicon derivatized at room temperature with (b) decylmagnesium bromide for 2 h and quenched with HCl in ether, (c) 4-fluorophenylmagnesium bromide for 2 h and quenched with HCl in ether, (d) decylmagnesium bromide for 1 h and quenched with $\text{CH}_3\text{CO}_2\text{D}$, and (e) decylmagnesium bromide for 1 h that was quenched with acetyl chloride and subsequently exposed to $\text{CH}_3\text{CO}_2\text{D}$. The peaks marked with asterisks (*) in c are for the 4-fluorophenyl species.

Figure 1c shows the IR spectrum for porous silicon that was exposed to 0.5 M 4-fluorophenylmagnesium bromide in THF for 2 h at 25 °C and subsequently quenched by addition of 1 M HCl in ether. The spectrum contains phenyl peaks at 1591, 1498, 1245, and 1165 cm^{-1} that correspond to a 4-fluorophenyl species.¹⁰ The XPS spectrum for the derivatized surface displayed peaks due to two types of fluorine and three types of carbon and no detectable magnesium and bromide signals (Figure 2).¹¹ The intensities of the carbon and fluorine peaks in the XPS spectrum were roughly those expected based on stoichiometry ($\text{F/C} = 1:7$ vs $1:6$; $\text{C}_\text{F}/\text{C}_\text{Si}/\text{C}_\text{tot} = 1:1:9$ vs $1:1:6$). The spectral characteristics of the Si(2p) region revealed little (or no) formation of silicon

(10) (a) Lin-Vien, D. *The Handbook of Infrared and Raman Characteristic Frequencies of Organic Molecules*; Academic Press: Boston, MA, 1991; Chapter 17. (b) Pouchert, C. J. *The Aldrich Library of FT-IR Spectra*; Aldrich Chemical Co.: Milwaukee, WI, 1985.

(11) In Figure 2 (insets), the peaks at 686.9 and 688.0 eV are assigned to fluorine atoms bonded to silicon and carbon, respectively, and the peaks at 284.3, 285.3, and 287.4 eV are assigned to carbon atoms where the peaks at highest and lowest binding energies are carbon atoms bonded to fluorine and silicon, respectively.

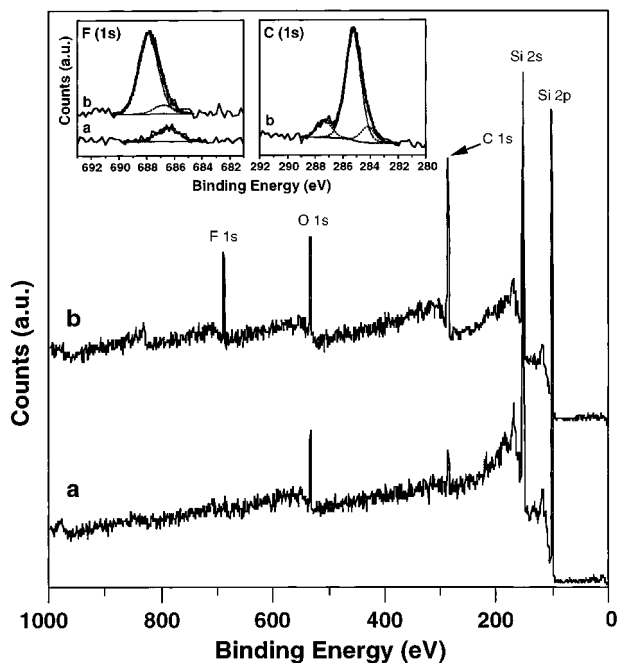
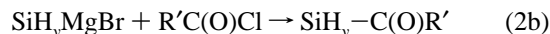


Figure 2. X-ray photoelectron spectra for porous Si (a) before and (b) after derivatization with 4-fluorophenylmagnesium bromide at room temperature for 2 h and quenched with HCl in ether. Dotted lines are based on deconvolution of the spectra into their component peaks.¹¹

oxides during the reaction of porous silicon with the Grignard reagents. Derivatized samples exposed to ultrahigh vacuum, HF acid/ethanol, and/or sonication in toluene (2×5 min) exhibited no change in the IR and XPS characteristics for the adsorbed species from those before these treatments. This stability suggests the formation of robust, covalently attached species to the silicon surface. The resistance of the layers to 48% HF acid(aq)/EtOH (1:1) provided further indication that the Grignard reagents form Si–C (and not Si–OR) linkages at the surface. The reactions proceeded to a saturation coverage and exhibited no further change upon extended exposure to the Grignard solution. The Grignard derivatization of porous silicon has the advantage over the use of alcohols to derivatize porous silicon as the latter method requires elevated temperatures (45–90 °C), and it degrades the surface during extended exposure to the reagents.²

Figure 1d displays the IR spectrum for porous Si treated with decylmagnesium bromide (1 M in THF) for 2 h at room temperature and quenched with $\text{CH}_3\text{CO}_2\text{D}$. The spectrum is similar to that in Figure 1b with the notable addition of a peak at 1515 cm^{-1} due to the formation of Si–D.^{2,4} We rationalize the generation of the Si–D species as a result of silyl anions formed from the breakage of Si–Si bonds by the attacking Grignard reagent; for comparison, Si–D species were not produced in control

experiments when porous Si was treated only with $\text{CH}_3\text{CO}_2\text{D}$ for similar periods of time. That Si–D species did not form by exposure to just $\text{CH}_3\text{CO}_2\text{D}$ but required reaction with Grignard reagents previous to this exposure suggests that the formation of the covalently attached organic layer does not proceed by a reaction that substitutes Si–H bonds with Si–C bonds (as for a hydrosilation process⁷) but instead proceeds by opening new sites on the Si surface (eq 1)¹² that are then available for substitution (eq 2a). This mechanism would proceed with attachment of organic species to the surface and relatively little change in the amount of Si–H termination, as seen by IR (Figure 1).



The formation of surficial silyl anions by the Grignard reagent was further suggested by the observation that porous silicon sequentially treated with decylmagnesium bromide, THF as wash at -78 °C (3×2 mL), acetyl chloride (neat or 1 M in THF), and $\text{CH}_3\text{CO}_2\text{D}$ shows peaks at 1648 and 1750 cm^{-1} and no Si–D peak at 1515 cm^{-1} (Figure 1e). We assign the 1648 cm^{-1} peak to the formation of surficial acylsilyl species that were produced by reaction between the acyl chloride and the generated surficial silyl anions (eq 2b),¹³ no peaks in the carbonyl region were observed when porous silicon was treated with acetyl chloride under these reactions conditions without an immediately preceding exposure to a Grignard reagent. When porous silicon was reacted with decylmagnesium bromide and quenched with undecenyl chloride, the DRIFT spectrum (see the Supporting Information) exhibited a peak at 1643 cm^{-1} due to the acylsilane C=O and vinyl C=C stretching modes and at 3080 cm^{-1} for the vinyl C–H stretching mode that are not present in Figure 1b. The assignment of the 1643 cm^{-1} mode to the acylsilane C=O stretching was based on its enhanced integrated intensity in this sample when compared to a porous silicon sample derivatized with undecylenic magnesium bromide and quenched with acid.¹⁴ The reaction of Grignard-treated porous silicon with acid chlorides produced samples that consistently exhibited a peak at ~ 1645 cm^{-1} in their IR spectra regardless of the Grignard reagent used. The generation of the surficial silyl anions is an interesting result of the Grignard reaction, and these reactive intermediates may provide sites for attaching other types of electrophiles onto the silicon surface.

As interest in porous silicon is largely due to the ability of this material to photoluminesce, we have begun examining the photoluminescent properties of these modified porous silicon samples. After derivatization, the porous silicon samples continued to exhibit photoluminescent behavior, with only small changes in the resulting photoluminescent intensities being observed for derivatizations with decyl and 4-fluorophenylmagnesium bromides (see the Supporting Information). The origin of these changes and the relationships between the chemical structure of attached species and the photoluminescent properties of the modified porous silicon are currently being investigated in our laboratory.¹⁵

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Supporting Information Available: Experimental details, diffuse reflectance IR spectra for porous Si derivatized with undecylenic MgBr/HCl and decylmagnesium bromide/undecenyl chloride, and photoluminescent spectra for porous silicon before and after modification with decylmagnesium bromide (5 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

(12) This reaction is proposed by analogy to the breakage of Si–Si bonds that occurs during the etching of silicon by weak nucleophiles such as alcohols at elevated temperatures.²

(13) (a) Brook, A. G.; Harris, J. W.; Lennon, J.; Sheikh, M. E. *J. Am. Chem. Soc.* **1979**, *101*, 83–95. (b) Capperucci, A.; Degl'Innocenti, A.; Faggi, C.; Ricci, A.; Dembech, P.; Seconi, G. *J. Org. Chem.* **1988**, *53*, 3612–3614.

(14) The area ratio between the peak at 1643 cm^{-1} and the peak at 3080 cm^{-1} was $\sim 6:1$ for porous silicon reacted sequentially with decylmagnesium bromide and undecenyl chloride and only $\sim 0.6:1$ for porous silicon derivatized with undecylenic magnesium bromide and quenched by acid. We ascribe this difference to the formation of an acylsilane species for the former case. The relevant IR spectra are included in the Supporting Information.

(15) We have also applied these reactions to the functionalization of nonporous, H-terminated Si surfaces and observed that 4-fluorophenylmagnesium bromide reacts at room temperature with HF-etched Si(100) and produces a robust organic film with a surface coverage of $\sim 50\%$ compared to that for a self-assembled monolayer of 4-fluorothiophenol on gold (determined using the F(1s) signal in XPS).