

Using Porous Silicon as a Hydrogenating Agent: Derivatization of the Surface of Luminescent Nanocrystalline Silicon with Benzoquinone

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Porous Si is a high surface area material produced by electrochemically etching single-crystal silicon in HF-containing electrolytes. It consists of a large number of interconnected Si nanocrystallites with a surface that is almost entirely covered with hydrogen atoms.^{1–7} By analogy with molecular compounds containing the Si–H moiety, the hydrogen atoms on the surface of porous Si should behave chemically as H[–] or H[•] species, although this reactivity pattern has never been clearly demonstrated. Under the appropriate conditions, porous Si samples can liberate H₂ from aqueous solutions,⁸ and the involvement of an H[–] surface species has been inferred from such observations. A variety of chemical or electrochemical reactions that modify Si surfaces have also been demonstrated, most of which involve Si–Si bond cleavage, oxidation, or halogenation as an initial step.^{9–20} The high surface area of porous Si makes it a promising candidate for stoichiometric or catalytic heterogeneous hydrosilylation reactions, though at present no examples of this reaction exist. In this work we demonstrate for the first time the hydrogenation of a chemical reagent utilizing the hydrogen atoms attached to a Si surface. We also show that this reaction can be used to tune the sensor properties of porous Si by modifying the photoluminescence quenching efficiency of the material in the presence of water or benzene vapor.

Nanocrystalline porous Si was prepared by anodic (two-electrode) photoelectrochemical etch of polished (100) n-type Si (0.64 Ω-cm) in a 1:1 48% aqueous HF:95% CH₃CH₂OH

electrolyte. The spectroelectrochemical cell was constructed of Teflon with the appropriate holes and mountings to allow acquisition of transmission infrared and backscattered photoluminescence spectra, and a coiled Pt wire was used as a counter electrode. The samples were etched for 30 min at 4 mA/cm², followed by a 5 min etch at 40 mA/cm². The 5 min post-etch step was used to impart higher porosity to the porous Si samples, which were typically 40–80% porous (measured by weighing several representative samples before etch, after etch, and after complete dissolution of the porous layer by treatment with 1.0 M aqueous NaOH). The samples were illuminated with approximately 5 mW/cm² white light from a tungsten filament source for the duration of the etching procedure. After etching, the cell was washed thoroughly with CH₂Cl₂ and dried under a N₂ stream. The surface of the resulting porous Si material is H-terminated and is characterized by infrared absorptions assigned to Si–H_x stretches around 2100 cm^{–1} and a Si–H₂ scissor mode at 915 cm^{–1} (Figure 1).^{1–3}

Exposure of porous Si to a 0.02 M toluene (or tetrahydrofuran) solution of 1,4-benzoquinone for 30 min and removal of the solution results in a new surface which displays bands in the infrared spectrum characteristic of a surface-bound *p*-hydroxylphenoxy (hydroquinone) moiety as depicted in Figure 1. The absence of a carbonyl C–O stretch at 1660 cm^{–1} indicates that the quinone is not present on the Si surface. In addition to the vibrational bands associated with the surface-bound hydroquinone moiety, new bands assigned to ν(Si–H) are observed at 2269 and 2203 cm^{–1}. These higher energy Si–H vibrations are characteristic of Si–H species that have O atoms bound to the Si atom² and probably arise from both surface oxide and the surface-bound hydroquinone. The derivatization reaction was carried out in the same spectroelectrochemical cell used for etching (open to air), and the solution was removed and the cell thoroughly rinsed with the toluene or tetrahydrofuran solvent before spectroscopic analysis. The absorptions assigned to surface-bound hydroquinone are retained after exposure to vacuum and thorough washing with ethanol, methanol, H₂O, or CH₂Cl₂, although the signals disappear upon soaking in acidic solution for several minutes. Similar results were obtained on treatment of *p*-type porous Si samples with benzoquinone.

Samples derivatized in a more polar solvent (tetrahydrofuran) or under irradiation (435 nm Hg emission line) proceeded with slightly faster (ca. 2×) rates, measured by monitoring the intensity of the characteristic absorptions in the infrared spectra. It has been shown that promotion of 1,4-benzoquinone to its triplet excited state enhances the rate of H[•] abstraction from solvent molecules,²¹ and both H[–] and H[•] abstraction mechanisms have been invoked in the reactions of quinones.^{22–24} Although the enhancement of the derivatization rate in polar solvents observed in the present study suggests hydride abstraction from surface Si–H species as outlined in Scheme 1, the data available at this time cannot rule out a hydrogen atom abstraction mechanism. An H[–] transfer mechanism has been suggested for the reactions of molecular organosilicon hydrides with quinones.²⁴

It should be noted that the mechanism proposed in Scheme 1 also requires rotation of the semiquinone anion after H[–] abstraction to allow formation of the Si–O bond. From the available data it cannot be determined if this occurs at the same Si atom at which H[–] abstraction occurs or if the semiquinone anion diffuses around on the surface before it attaches.

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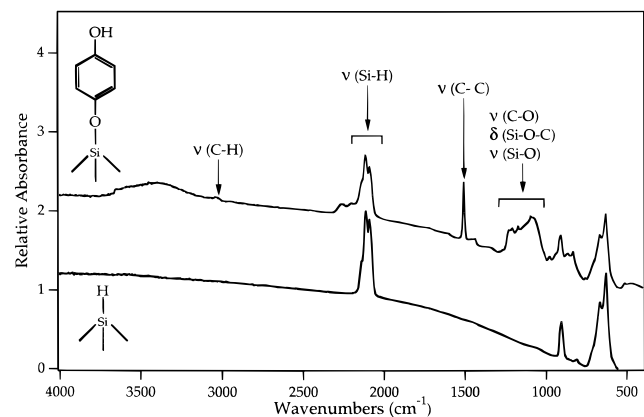
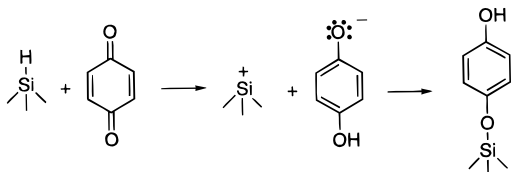


Figure 1. Fourier-transform infrared absorbance spectra of a porous Si sample before and after derivatization. Bottom: As-formed (HF etched) porous Si showing bands assigned to $\nu_{(\text{Si-H})}$ of the surface hydrides. Top: Sample after treatment with benzoquinone, showing the appearance of bands characteristic of a surface-bound hydroquinone moiety; $\nu_{(\text{C-C})}$ ring stretching mode at 1518 cm^{-1} , broad $\nu_{(\text{O-H})}$ band at 3414 cm^{-1} , aromatic $\nu_{(\text{C-H})}$ at 3052 cm^{-1} , and bands at 1229 , 1176 , and 1091 cm^{-1} assigned to $\nu_{(\text{C-O})}$ stretching, $\delta_{(\text{Si-O-C})}$ bending and $\nu_{(\text{Si-O})}$ stretching vibrations. The top spectrum is offset from the bottom one by 1.0 absorbance units for clarity. The spectra were obtained in a spectroelectrochemical cell constructed of Teflon with the appropriate holes and mountings to allow acquisition of transmission infrared spectra without altering the sample position.

Scheme 1



The intensity of the steady-state photoluminescence spectrum of hydroquinone-derivatized porous Si is reduced to $14\% \pm 2\%$ of the original (freshly etched) porous Si. There is a concomitant decrease in the lifetime of the time-resolved photoluminescence spectrum (see Supporting Information). Soaking the derivatized wafer in a solution of $\text{HCl}/\text{H}_2\text{O}/\text{CH}_3\text{-CH}_2\text{OH}$ removes $>60\%$ of the hydroquinone and results in an increase in silicon oxide-related absorptions in the infrared spectrum. Removal of the hydroquinone species also results in recovery of the steady-state photoluminescence intensity and the photoluminescence lifetime²⁵ to within 85% of the original (H-terminated porous Si) values.

The photoluminescent properties of nanocrystalline porous Si are of interest for sensor applications. In previous contributions we have demonstrated that chemical or electrochemical derivatization reactions can modify the ability of porous Si to sense gases such as H_2O , benzene, or ethanol.^{14,15,17,26} A general conclusion from these studies has been that reactions which impart a degree of hydrophilicity to the porous Si surface increase the ability of H_2O to quench the photoluminescence from the material. Similar results are observed for hydro-

(25) Due to the nonexponential character of the luminescence decay curve for porous Si, it is not possible to extract a single exponential lifetime from the data. Instead, an effective half-life was calculated by determining the time at which the area under the decay curve is half of the total area.

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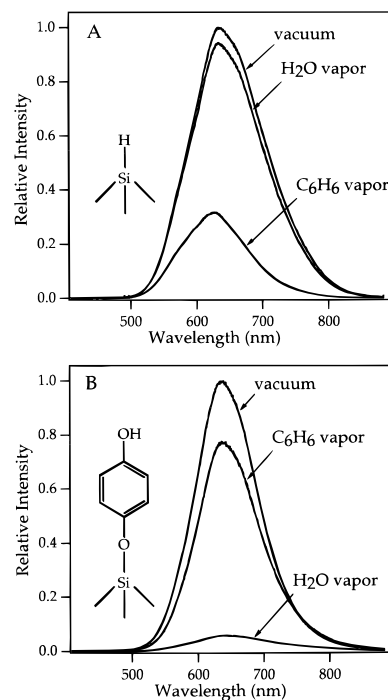


Figure 2. Steady-state spectra of as formed (A) and derivatized (B) porous Si comparing photoluminescence quenching of benzene (90 Torr) and water (21 Torr) vapors relative to vacuum as indicated. Derivatization of the porous silicon surface with hydroquinone imparts a greater sensitivity to water vapor and reduces the sensitivity to benzene. The quenching process for both samples is reversible; evacuation of the chamber results in recovery of the photoluminescence spectrum to the “vacuum” trace reproducibly for >15 cycles.

quinone-terminated porous Si. Thus H_2O vapor quenches $86\% \pm 2\%$ of the photoluminescence from a hydroquinone-substituted material, but it only quenches $3\% \pm 1\%$ of the photoluminescence from the original hydride-terminated material (Figure 2). In contrast, benzene vapor quenches the photoluminescence of the hydrophilic, hydroquinone-terminated material by only $26\% \pm 2\%$, whereas it quenches $70\% \pm 2\%$ of the photoluminescence from the hydrophobic, hydride-terminated material (Figure 2). The fact that the relative sensitivity to these molecular adsorbates reverses upon surface derivatization indicates that the derivatization reaction induces a fundamental change in the rate of one or both quenching pathways. If the relative quenching rates were not modified, the degree of steady-state quenching would merely scale with the photoluminescence lifetime of each sample.

The data presented here provide a new route to chemically modify Si surfaces by using the surface hydrides as a reagent. The reaction is mild enough to preserve the photoluminescence of the Si nanocrystallites and to selectively tune their photoluminescence quenching response.

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Supporting Information Available: Time-resolved and steady-state photoluminescence spectra obtained from a porous silicon sample before and after derivatization with benzoquinone (2 pages). See any current masthead page for ordering and Internet access instructions.

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