J. Am. Chem. Soc. **1995,** *117,* 8295−8296

Photoderivatization of the Surface of Luminescent Porous Silicon with Formic Acid

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Received May 15, 1995

Modification of technologically important surfaces is currently an active field of research. Important examples include silyl halides on SiO_2,[1] carboxylic acids on metal oxides,[2] thiols on Au[3] or GaAs,[4] organophosphates on oxides,[5] and recently, alkanes on Si.[6] In this work, we report a new reaction scheme for functionalizing Si surfaces by light-induced reactions. The Si used in this report was etched in HF to prepare a porous layer several microns deep.[7] The advantage of using porous Si is that it has a very large surface area which greatly aids spectroscopic identification of surface composition. Furthermore, the visible photoluminescence of porous Si is sensitive to physisorbed and chemisorbed species, allowing for an additional probe of the chemical nature of the surface.

The Si porous layer was made by anodically etching n-type Si(100) (0.03−0.05 Ω-cm) with 1:1 49% HF(aqueous)/CH_3CH_2OH in a Teflon etch cell. The counter electrode was a coiled Pt wire. The etch conditions were 100 mA/cm^2 for 2−3 min under 15 mW/cm^2 white light from a tungsten filament source. After etching, the samples were washed with CH_2Cl_2 and thoroughly dried under a N_2 stream. The resulting surface is hydride terminated. Diffuse reflectance Fourier-transform infrared spectroscopy (DRIFTS) identified strong absorptions assigned to $Si-H_x$ stretches around 2100 cm^{-1} and a $Si-H_2$ scissor mode at 915 cm^{-1}, Figure 1a.[8]

The porous Si samples were derivatized in neat HCOOH containing 1 M HCOONa in the same Teflon container used for the HF etch. A bias of +0.3 V was applied to the Si working electrode relative to the Pt counter electrode (Si reverse-biased), in the presence of white light to generate a photocurrent of 2−3 mA/cm^2. The photocurrent dropped to half its initial value over a period of several minutes. A small amount of gas was evolved, indicating that the current may be due to decomposition of the acid by a Kolbe-type reaction.[9] After 10 min the sample was removed and washed with formic acid and CH_2Cl_2. The sample was then dried under a N_2 stream and placed under vacuum.

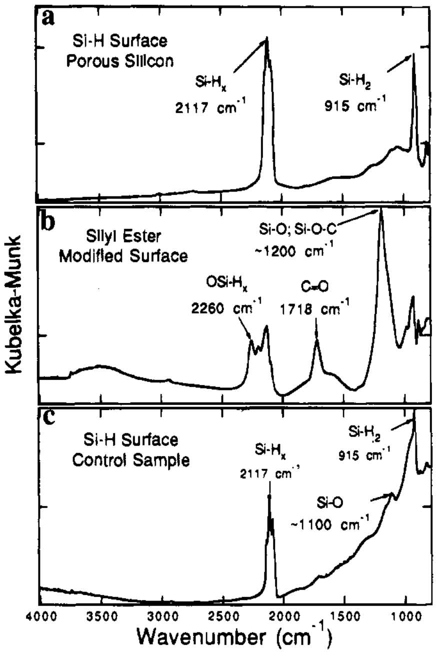

Figure 1. Diffuse reflectance FTIR spectra of porous Si surfaces: (a) as-formed (HF etched) porous Si showing strong $Si-H_x$ absorptions; (b) ester-modified surface; (c) sample treated identically to that in panel b but without illumination; this spectrum shows little or no evidence of silyl esters.

The resulting derivatized surface was identified by DRIFTS, Figure 1b. The surface silyl ester is identified by the ν(CO) stretching vibration at 1716 ± 2 cm^{-1}. By comparison, the carbonyl C−O stretch of free formic acid occurs at 1720 cm^{-1}, and molecular silyl esters have ν(CO) in the 1700−1770 cm^{-1} region (for example, ν(CO) of $(CH_3CH_2)_3SiOOCCH_3$ occurs at 1720 cm^{-1}).[10] The Si is oxidized, as identified by a broad band around 1200 cm^{-1}, assigned to Si−O stretching and Si−O−C bending vibrations. An additional $Si-H_x$ stretching mode is observed at 2260 cm^{-1}, assigned to ν(Si−H) from Si bonded to the formate ester. This frequency is slightly higher than the value of ν(Si−H) typically observed on oxidized Si (2254 cm^{-1}),[8] as expected from the greater inductive ability of the ester,[10] and is an indication that the back-bonded O is associated with the surface-bound ester species, though some surface oxide may be present as well. The absorptions assigned to the silyl ester persist after exposure to vacuum and thorough washing with alcohols, H_2O and CH_2Cl_2, although the signals disappear slowly upon soaking in water or alcohol for several hours. Molecular silyl esters are known to transesterify upon exposure to alcohols or H_2O.[11]

A reference sample was prepared by treating porous Si under identical conditions with the exception that it was not exposed to light. The current in the dark was <0.05 mA/cm^2. This sample showed no sign of ester formation, possessing only the Si−H stretching vibrations of the starting porous Si, Figure 1c.

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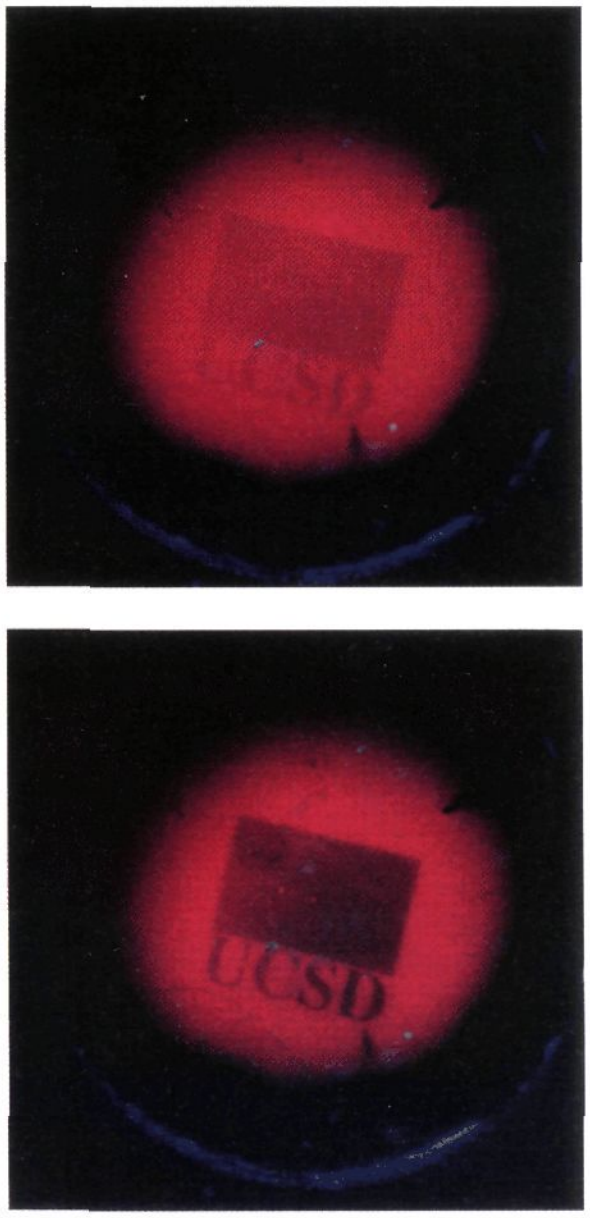
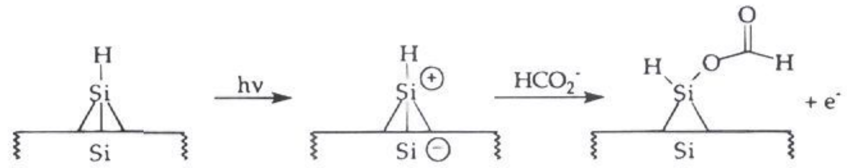


Figure 2. Photographs of the red PL (excitation with 365 nm light) from a circular (1 cm diameter) porous Si sample showing photopatterned square and lettering where the Si surface has been modified with silyl esters. Top (a): Sample in vacuum. The photopatterned square is somewhat discernible due to the lower PL quantum yield of the ester-modified porous silicon. Bottom (b): The same sample in the presence of H_2O vapor. The intensity of emission from the nonderivatized Si−H surface is relatively unaffected by the water vapor (10−20% quenched). PL from the region patterned with the hydrophilic ester functionality is quenched by >60%.

Similarly, porous Si immersed in the formate electrolyte and illuminated at open circuit showed little or no sign of modification of the native Si−H surface. Thus the species observed on derivatized porous Si is not due to adsorbed formic acid or sodium formate. Formate bound to Si in a bidentate fashion can also be ruled out because such species would have ν(CO) stretches at a much lower energy and O−C−O symmetric and antisymmetric vibrational modes,[2] none of which were observed. The single observed stretching mode indicates that the species is an ester, and the energy of the stretch falls within the range expected for silyl esters.

The integrated intensities of Si−H and OSi−H IR absorptions do not decrease after derivatization, indicating that the Si−ester bond is formed by breaking Si−Si bonds, Scheme 1.

Scheme 1



Porous Si can be photopatterned by illuminating the surface through a mask during the derivatization procedure. Photoluminescence (PL) from photopatterned surfaces is shown in the photographs in Figure 2. The photopatterned square and letters can be identified by their slightly lower emission intensity in Figure 2a. IR spectroscopy identified the less emissive area as that possessing the silyl ester surface.

It has previously been shown that the intensity of PL from porous Si is reversibly quenched by molecular adsorbates, and that the sensitivity can be tuned via surface modification.[12,13] In the present work, photoelectrochemical generation of the silyl ester surface rendered the porous Si PL susceptible to reversible quenching by H_2O vapor. By comparison, PL from nonderivatized porous Si is quenched only slightly by H_2O vapor due to the hydrophobic nature of the Si−H surface.[12] Thus the contrast between the derivatized and nonderivatized regions of Figure 2 increases upon exposure of the entire surface to water vapor (Figure 2b), relative to the sample in vacuum (Figure 2a). This work demonstrates photolithographic modification of a Si surface at the molecular level and the effect of such modification on properties such as carrier recombination rates and surface hydrophilicity.

Acknowledgment. This work was funded by the National Science Foundation. J.S.H. was supported by an NSF Research Experience for Undergraduates Fellowship.

Supporting Information Available: Detailed description of electrochemical experimental conditions, diagram of etch bath, IR spectra of a photopatterned sample, and emission spectra in vacuum and H_2O vapor (4 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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