Thermal Derivatization of Porous Silicon with Alcohols

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The modification of semiconductor surfaces by chemisorptive strategies remains an active area of research.[1−3] These efforts are directed toward the introduction of electroactive and functional groups on their surfaces and the stabilization of the electronic and/or optical properties of the semiconductor. Porous silicon has become a material of recent technological interest due to its photo- and electroluminescent properties and possible compatibility with existing silicon-processing strategies.[4] Methods that can derivatize the surface of porous silicon may allow the tailoring of its interfacial properties and provide protection against corrosive processes that can diminish its luminescence. In this paper, we report that the surface of porous silicon can be readily derivatized by reaction with alcohols to form a covalently attached layer. The reaction appears to be highly flexible and overcomes the limitations associated with reported methods for modifying this material.[5−10] Our procedure is analogous to methods used for preparing self-assembled monolayers,[11] except that we require the use of anaerobic, anhydrous conditions and modest heating. The method produces robust organic films on porous silicon that rely on covalent attachment.

We prepared porous silicon by anodically etching a 50 mm diameter, p-type Si(100) wafer (1−10 W cm) with 1:1 48% HF(aqueous)/EtOH in a Teflon cell. The etch conditions were 30 mA/cm^2 for 20 min and used a Pt mesh counterelectrode; these conditions produce a hydrogen-terminated layer of porous silicon on the silicon substrate. After etching, the samples were rinsed with EtOH, dried in a stream of N_2, and stored in a dessicator before use. The porous silicon samples were derivatized in neat alcohol or a solution in anhydrous dioxane (0.1 M) at temperatures between 20 and 90 °C under an atmosphere of N_2. Reaction times varied between 0.5 and 24 h depending on the reaction temperature, the concentration, and the reaction rate for the alcohol. After reaction, the porous silicon sample
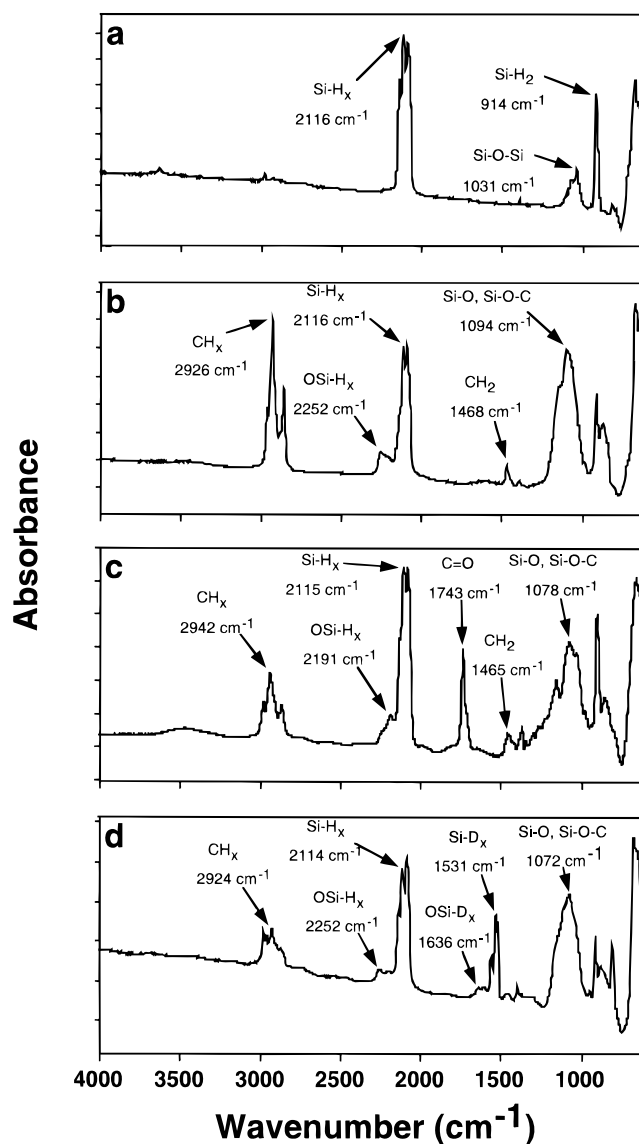

Figure 1. Diffuse reflectance infrared spectra for (a) underivatized porous silicon and porous silicon functionalized with (b) undecanol at 87 °C for 1 h, (c) ethyl 6-hydroxyhexanoate at 87 °C for 20 min, and (d) CH_3CH_2OD at 45 °C for 1 h.[12]

was rinsed with EtOH and dried thoroughly under a stream of N_2. The stabilities of some layers were examined by characterizing them before and after sonication in THF (2 × 5 min).

Figure 1a displays a diffuse reflectance infrared Fourier-transform spectrum (DRIFTS) for the porous silicon substrate prior to derivatization with alcohol. The spectrum contains absorptions for $Si−H_x$ stretches at 2116 cm^{-1}, for Si−O−Si stretch at 1031 cm^{-1}, and for $Si−H_2$ bending at 914 cm^{-1}.[12,13] After exposure of the porous Si to undecanol at 87 °C for 1 h, the DRIFT spectrum (Figure 1b) exhibited peaks at 2857−2959 cm^{-1} due to the C−H-stretching modes of the alkyl chain, changes in the Si−H-stretching region (2089−2137 cm^{-1}) that are consistent with the formation of $OSiH_x$ species, and increased intensity at ∼1100 cm^{-1} that is due to Si−O−C modes. The greatest change to the Si−H-stretching region upon reaction with the alcohol was the diminished intensity at 2139 cm^{-1} for SiH$_3$ species relative to the changes for SiH (2089 cm^{-1}) and SiH$_2$ species (2115 cm^{-1}). This observation suggests that the SiH$_3$ species are either more reactive or are removed from the surface

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(10) The adsorbed species reported to date on porous silicon are limited to CH_3O,[5,6] HCO_2,[7,8] CH_3CO_2,[8] CF_3CO_2,[8] and $CH_3CH_2CH_2O$.[9] Available methods require the use of UV irradiation[7−9] or that the adsorbate be volatile (for assembly under ultrahigh vacuum)[5] or have a high dielectric constant (for derivatizations performed electrochemically).[6−8]

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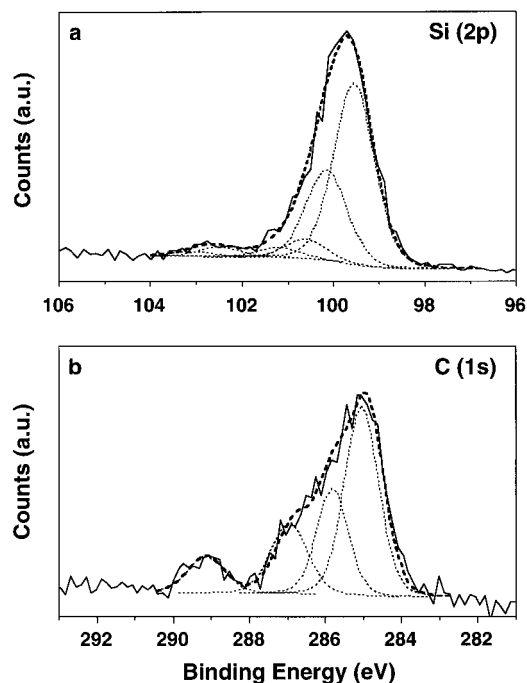
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Figure 2. X-ray photoelectron spectra for porous silicon derivatized with ethyl 6-hydroxyhexanoate at 87 °C for 20 min: (a) Si(2p) region and (b) C(1s) region. The dotted lines are based on deconvolution of the spectra (solid line) into their component peaks. In b, the peak at the highest binding energy is to due to the carbonyl.

during reaction. The presence of undecanol in a physisorbed state is ruled out by the lack of intensity at $\sim$3400 cm^{-1} for the OH-stretching mode of the free adsorbate (see Supporting Information).[14] The absorptions in the spectra persist after exposure of the sample to vacuum and rinsing and/or sonication with THF. The results demonstrate that this process forms a covalently attached layer to the porous silicon surface.

We have used this method to attach a range of alcohols onto porous silicon, including phenol, 3-phenylpropanol, 10-undecenol, 11-bromoundecanol, ethyl glycolate, and ethyl 6-hydroxyhexanoate. In each case, DRIFT spectra contained absorbances that were compatible with the attachment of the adsorbate. For example, aromatic modes were observed for phenol and 3-phenylpropanol, vinyl modes for 10-undecenol, methyl modes for undecanol, and a C=O-stretching peak for ethyl glycolate and ethyl 6-hydroxyhexanoate. For the ethyl 6-hydroxyhexanoate, the spectra exhibited similar absorbances as those observed upon adsorption of undecanol with an additional peak at 1743 cm^{-1} for the the C=O-stretching mode of the ester (Figure 1c).[15] In each of these cases, the spectra exhibited absorptions characteristic of the free molecule with the exception of low (or no) intensity for the OH-stretching mode after their attachment to the porous silicon surface.[14]

Analysis of the derivatized substrates by X-ray photoelectron spectroscopy (XPS) demonstrated that the adsorption of the alcohol occurs without little formation of surface oxides (Figure 2a). XPS spectra for the derivatized samples of porous silicon contained peaks due only to C, O, and Si, except for the sample derivatized with 11-bromoundecanol that also displayed peaks due to Br. Figure 2b shows the C(1s) spectrum for porous silicon derivatized with ethyl 6-hydroxyhexanoate. Here, the

C(1s) spectrum exhibits peaks due to the carbonyl carbon, carbons adjacent to polar species, and the remaining carbon units. The relative ratios of these peaks are consistent with ethyl 6-hydroxyhexanoate being the predominant carbonaceous species on the porous silicon surface.[16] XPS spectra of the functionalized samples indicate that the layers readily survive ultrahigh vacuum conditions and provide further evidence that the layers are covalently attached to the surface.

We further explored the surface chemistry of this process by reacting porous silicon with CH$_3$CH$_2$OD (Figure 1d). DRIFT spectra for porous silicon that was exposed to CH$_3$CH$_2$OD for 1 h at 45 °C displayed peaks at 1517$-$1636 cm^{-1} that are due to Si$-$D bonds. The formation of Si$-$D in this reaction suggests that reaction between alcohols and the porous silicon surface occurs with cleavage of Si$-$Si bonds providing sites for covalent attachment. Direct isotopic exchange between the CH$_3$CH$_2$OD and SiH species is unlikely due to the poor lability of the SiH group.[5]

$$H_xSi-SiH_y + ROH \rightarrow H_xSiOR + SiH_yH$$
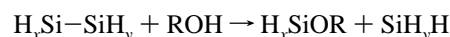
Further evidence for this reaction is based on the observation that extended exposure of porous silicon to the alcohol can result in its dissolution.[17] This observation suggests that the reaction between porous silicon and alcohol to form covalent layers on the porous silicon surface may have analogies to a controlled etching process where the reaction products are alkoxysilanes. Similar etching processes have been identified to operate in the formation of self-assembled layers on gold and silver using alkanethiols as adsorbates.[18,19]

We have also begun examination of the effect of this derivatization on the photoluminescent properties of the porous silicon. In general, these modifications produced no change in the frequency of the emitted light or its intensity after derivatization, regardless of the alcohol.[17] We are presently examining the abilities of these alkyl films to provide some resistance for the porous silicon against oxidation and loss of its luminescent properties. Additionally, we find that these procedures can be used to derivatize crystalline silicon substrates at roughly monolayer coverages with the notable advantages over porous silicon that the reaction proceeds without degradation or oxidation of the silicon support (see Supporting Information). Further work to develop these procedures for this substrate are underway.

Supporting Information Available: Infrared spectra for undecanol and ethyl 6-hydroxyhexanoate (for comparison with Figure 1b,c) and an X-ray photoelectron spectrum for crystalline silicon derivatized with ethyl 6-hydroxyhexanoate (for comparison with Figure 2a) (3 pages). See any current masthead page for ordering and Internet access instructions.

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(14) In the spectra of neat undecanol and ethyl 6-hydroxyhexanoate, the intensities of the OH-stretching mode at $\sim$3400 cm^{-1} are $\sim$0.5$\times$ that of the most intense CH-stretching mode, γ_a(CH$_2$), for the former and $\sim$0.5$\times$ that of the C=O stretch for the latter. The Supporting Information provide these spectra for comparison.

(15) The position for the carbonyl stretch is $\sim$10 cm^{-1} higher in the adsorbed state due to the absence of hydrogen bonding with the hydroxyl group.

(16) In Figure 2b, the relative intensity of the carbonyl peak to that for the rest of the C(1s) spectrum (1:10) is close to its carbon ratio (1:7) for the adsorbate.

(17) We have observed that exposure of the porous silicon to neat undecanol at 87 °C for times longer than 3 h results in degradation of the porous silicon as evidenced by its loss of structural integrity. Lower concentrations ($\sim$20 h, 0.1 M in dioxane) and temperatures ($\sim$6 h at 45 °C) slowed this process. The loss of material occurs with a concurrent loss in photoluminescence.

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