Alkylation of Porous Silicon by Direct Reaction with Alkenes and Alkynes**

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Methods for the derivatization of silicon surfaces have generally relied upon reactions with the native oxide.[1] Recently, however, synthetic strategies for the fabrication of covalently bound monolayers have been developed which exploit the inherent reactivity of the hydrogen-terminated surface formed on fluoride etching.[2–9] Such a layer is also known to terminate the surface of photoluminescent porous silicon (PS), and associated molecular functionalization routes have also been reported for this material.[3] Cases of PS derivatization methods have, until recently, been limited to modification of the surface through the formation of Si–O-bonded films by reactions with, for example, alcohols and carboxylic acids.[4, 5] Methods for direct alkylation of silicon surfaces through Si–C bonds have now been reported by several workers,[2, 6–8] with one of these being for PS;[8a] such films have been shown to be very stable. To date these reactions with alkenes have generally relied upon catalysis (e.g. radical initiators, Pt complexes, $EtAlCl_2$) for reaction.[2, 6, 8a] Here we present the covalent modification of PS by direct reaction with unsaturated hydrocarbons *in the absence of catalyst.* The reaction, with alkenes or alkynes, can be carried out with either neat reagent or in dilute solution.

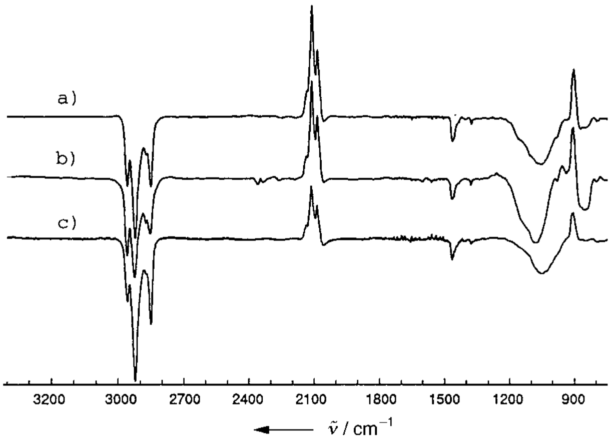

Figure 1. Transmission IR spectra of porous silicon after reaction with a) 1-octene (5 d), b) 1-octyne (1 d), and c) 1-undecene (5 d); 200 scans at a resolution of 4 cm^{-1}. All spectra were recorded relative to unmodified porous silicon.

Table 1. Assignment of the IR bands for modified PS (n.o. = not observed).

Assignment	Hexene/PS [cm^{-1}]	Octene/PS [cm^{-1}]	Undecene/PS [cm^{-1}]	Vinylferrocene/PS [cm^{-1}]	Octyne/PS [cm^{-1}]
$\nu(C{\equiv}CH)$	–	–	–	–	n.o.
$\nu_{Cp}(CH)$	–	–	–	3098	–
$\nu(C{=}CH_2)$	n.o.	n.o.	n.o.	n.o.	–
$\nu_a(CH_3)$	2961	2961	2961	n.o.	2961
$\nu_a(CH_2)$	2924	2924	2924	2920	2927
$\nu_s(CH_3)$	2878	2878	2878	n.o.	2878
$\nu_s(CH_2)$	2856	2854	2854	2850	2856
$\nu(C{\equiv}C)$	–	–	–	–	n.o.
$\nu(C{=}C)$	n.o.	n.o.	n.o.	n.o.	–
$\delta_a(CH)$	1466	1464	1464	–	1458
$\delta_s(CH_3)$	1381	1380	1380	–	1382
$\nu(CC)$	–	–	–	1107	–
$\delta(CH)$	–	–	–	1000	–
$\pi(CH)$	–	–	–	815	–

FT-IR spectra (Figure 1, Table 1) of PS samples after reaction with alkene or alkyne show bands for C–H stretching modes around 2900 cm^{-1} and C–H deformation modes at 1465 and 1380 cm^{-1} of alkyl chains attached to the silicon surface. The use of relatively volatile adsorbates minimized the possibility of physisorbed hydrocarbon remaining within the porous structure. In addition, strong bands due to the olefinic (or acetylenic) C–C stretch and C–H stretch and C–H deformation modes, present in the IR spectrum of the starting molecules, are absent in the spectra of the modified PS, indicating that rehybridization of the terminal alkene (alkyne) group from sp^2 (sp) to sp^3 has taken place. No intermediate olefinic species was observed, in contrast with the reported catalytic hydrosilylation route.[8] Loss of the major part of the hydrogen termination of the PS is evident from the negative bands for the $Si-H_x$ stretch modes around 2100 cm^{-1} and the $Si-H_2$ scissors mode at 915 cm^{-1}. This suggests that the reaction proceeds by abstraction of surface hydrogen rather than attack at Si–Si back bonds, which is in contrast to reported mechanisms for the reaction of PS with alcohols.[3, 4] Even after five days of reaction, the band for the $Si-H_x$ stretch retains up to 30% of its original intensity, indicating incomplete modification of the surface. This may be due to microporous regions of the PS which are inaccessible to hydrocarbon molecules of chain length C_6-C_{11}. Preferential loss of particular hydride species was not observed, which is in agreement with previous studies on PS modification.[4, 8, 10] The peak at 1050 cm^{-1} is assigned to the Si-O-Si asymmetric stretch. Earlier work has shown PS to be highly sensitive to oxidation under typical preparative conditions[3, 11] using normal Schlenk line procedures. Oxidation of the PS is therefore seen to compete with alkylation.[12]

To demonstrate that functional molecules can be attached to the surfaces vinylferrocene was used. Figure 2 shows a typical cyclic voltammogram (CV) of the ferrocenyl-modified porous silicon, and Figure 3 shows the dependence of the anodic peak current i_{pa} on the scan rate. The large anodic peak current is due to oxidation of ferrocene (Fc) moieties attached to the porous structure, and the relatively small cathodic peak current results from the reduction of Fc$^+$.[13] The latter is not simply due to the rectifying properties of the *p*-type semi-

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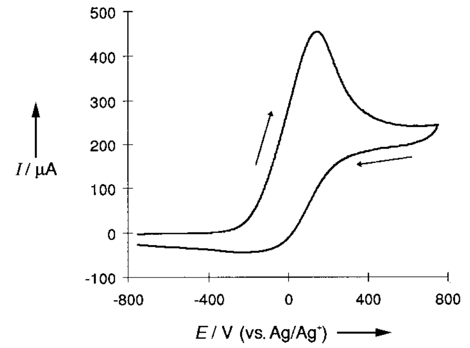

Figure 2. Cyclic voltammogram under ambient illumination of porous silicon (0.38 cm^2) after modification with vinylferrocene. The scan rate was 2 mV s^{-1}, the electrolyte was 0.1 M nBu$_4$NPF$_6$ in MeCN, and the reference electrode was Ag/0.01 M Ag$^+$.

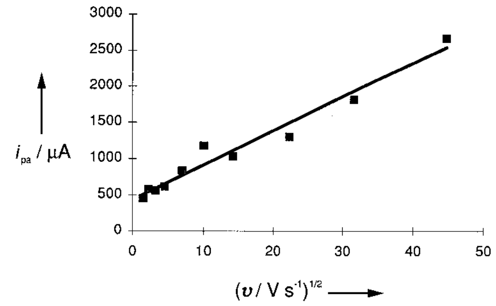

Figure 3. Dependence of the anodic peak current i_{pa} on $v^{1/2}$ for a ferrocenyl-modified PS layer. The electrolyte was 0.1M nBu$_4$NPF$_6$.

conductor–electrolyte interface since illumination (100-W tungsten–halogen lamp) produced no change in the CV. In addition, our previous work[9] has shown that nearly symmetrical surface waves for tethered ferrocenes are observed on silicon electrodes under ambient illumination. An alternative, loss of Fc$^+$ to the external solution, was not observed and is also inconsistent with the lack of a large decrease in i_{pa} with cycle number. Based on prior reports that Fc$^+$ has a redox potential sufficient to inject holes into single-crystal silicon,[14] we propose that the oxidized ferrocenes inject holes into silicon crystallites that are electrically isolated from the bulk of the semiconductor. The reaction scheme is then that described by Equations (1) and (2); Si$_n$ represents a silicon crystallite.

$$\text{at the silicon substrate:} \quad \mathrm{Fc} \rightarrow \mathrm{Fc}^+ + \mathrm{e}^- \tag{1}$$

$$\text{in the porous film:} \quad \mathrm{Fc}^+ + \mathrm{Si}_n^0 \rightarrow \mathrm{Fc} + \mathrm{Si}_n^+ \tag{2}$$

A linear dependence of i_{pa} on the square root of the scan rate, $v^{1/2}$ typical of a diffusional process was observed rather than the direct proportionality between i_{pa} and v expected for surface-confined electrochemistry.[13] However, such behavior is frequently observed in polymer-coated electrodes[15] when complete oxidation of all the redox centers (Fc groups) is not achieved due to slow charge/mass transport. This interpretation of the data in Figure 3 is also consistent with the high resistivity of porous silicon.[16]

Photoluminescence (PL) measurements showed that the PL of the PS samples was significantly quenched on alkylation with no shift in wavelength being observed. A decrease in PL emission intensity after modification is well documented and can be explained as being due to adsorbed surface species acting as nonradiative recombination centers.[3]

Stability tests on the 1-octene-modified PS (reaction time of five days) showed it to be significantly more robust than unmodified PS. No change in the IR spectra was observed after boiling in water and KOH solution (pH 12) for one hour. Unmodified PS has been shown to undergo substantial oxidation and degradation after such treatment.[8, 17] The use of ethanolic KOH solution (75 % KOH, 25 % ethanol, pH 12), however, led to stripping of the porous layer after one hour at room temperature due to increased pore wetting.[8a, 11] The linear n-octyl chain does not, therefore, provide the same degree of protection to the PS surface as does the more bulky *tert*-butyl group examined by Buriak and Allen.[8a]

In conclusion, porous silicon can be alkylated by direct reaction with unsaturated hydrocarbons and no catalyst. The Si–C-bound layers produced are significantly more robust than the Si–O-bound layers obtained by reaction of PS with alcohols, etc. This method also allows the attachment of chemically reactive groups such as redox agents onto the surface.

Experimental Section

Porous silicon was formed by galvanostatic anodization for 4 min of a p-doped Si(100) wafer (1–10 Ω cm) in a solution of 48 % aqueous HF and ethanol (50/50) in a Teflon cell with a current density of 19 mA cm^{-2}. The PS was then rinsed in deionized water (Millipore, 18 MΩ) to remove ethanol, immersed in 48 % aqueous HF to ensure removal of any remaining oxide, and finally rinsed in deionized water (20 s) and dried in a N$_2$ stream. A transmission FT-IR spectrum indicated that samples so prepared were hydrogen-terminated with little or no oxide present. These samples were then immersed in 1M solutions of 1-octene, 1-octyne, and 1-undecene (Aldrich, > 97 %) in toluene and heated at reflux (110–180 °C) typically for 18–20 h before analysis by FT-IR spectroscopy (Biorad FTS-60 spectrometer fitted with a narrow-band MCT detector). After reaction the samples were rinsed in toluene and dried under vacuum. Some hydrogen termination was still observed after reaction times of up to five days.

Ferrocenyl-derivatized porous silicon was also prepared by direct reaction of vinylferrocene (0.5M solution in toluene) with porous silicon. After washing with toluene and acetone to remove physisorbed material, the ferrocenyl-modified porous silicon was examined by CV (electrolyte: 0.1M nBu$_4$NPF$_6$ in MeCN). The reference electrode Ag/0.01 M AgNO$_3$ was separated from the working electrode by a fine glass frit.

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[10] The positive "tail" on the low-frequency side of the Si–H$_x$ stretching band below 2100 cm^{-1} may, however, indicate the formation of a less tightly bound surface hydride species in which the silicon atom is also bonded to an alkyl group [Eq. (3)]. Such a decrease in the Si–H

$$>SiH_2 + RCH{=}CH_2 \rightarrow >SiH(CH_2)_2R \qquad (3)$$

stretching frequency, with increasing alkyl substitution, has been observed previously for alkylsilanes; see, for example, G. Lucovsky, *Solid State Comm.* **1979**, *29*, 571–576.

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Olefin Metathesis of a Ruthenium Carbene Complex by Electrospray Ionization in the Gas Phase[**]

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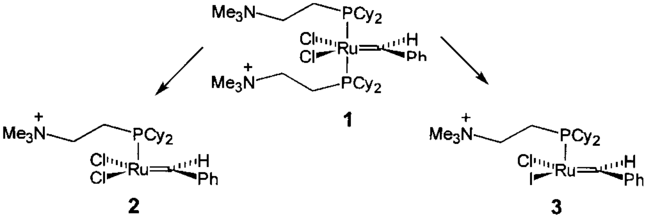
We report the direct mass spectrometric observation of an olefin metathesis reaction[1] of an acyclic alkene and the ring-opening metathesis (ROM) of cycloalkenes in the gas phase by the water-soluble ruthenium benzylidene complex **1** developed by Grubbs et al.[2] Besides constituting the first observation of olefin metathesis in the gas phase by a complex that performs the same reaction in solution, the mass spectrometric study finds and quantifies intramolecular π complexation of the penultimate double bond in the growing oligomeric chain to the metal center, and provides surprising evidence that, except for a large increase in the absolute rates, the gas phase reactions of a $[RuCl_2(=CHPh)(PR_2R')_2]$ complex closely parallel the corresponding reactions in solution.

The electrospray ionization[3, 4] tandem mass spectrometric (ESI-MS/MS) experiment was performed in a modified TSQ-7000 mass spectrometer (Finnigan MAT) as described in our reports on gas-phase C–H activation[5] by $[CpIr(PMe_3)(CH_3)]^+$, oxo-transfer reactions[6] by $[O{=}Mn^V(salen)]^+$ (salen = *N,N'*-bis(salicylidene)ethylenediamine dianion), the Ziegler–Natta polymerization[7] of α-olefins by $[Cp_2ZrR]^+$, and reversible hydrogenation of olefins[8] by $[Rh(PMe_3)_2]^+$. Complex **1** was synthesized as described by Grubbs et al.[2] A 10^{-5} M solution of the diiodide salt of **1** in CH_2Cl_2 was then electrosprayed. Ions were thermalized with about 10 mTorr inert gas in the first octopole region (Scheme 1).



Scheme 1. Reactions of **1** in the mass spectrometer. Cy = cyclohexyl.

Under relatively mild desolvation conditions, that is with a tube lens potential of 44 V in front of the first octopole, the mass spectrum consisted of signals due to the dication **1**, the monocation **2**, which was formed by the loss of one phosphane ligand from **1**, and a second monocation **3** with a mass that indicated that one of the chloride ligands in **2** had been replaced with an iodide. The use of the dichloride salt of **1** instead of the diiodide eliminated **3**. As the tube lens potential was increased stepwise to 150 V, first the intensity of the peak due to **2** increased at the expense of that for **1**, and then decreased with the loss of the second phosphane (the phosphane appears in the mass spectrum because it carries the charge on its side chain), loss of trimethylamine, and loss of HCl. These fragments are consistent with the assumed structure. When 1-butene was used as the thermalization gas, a new signal with the mass corresponding to the ruthenium propylidene product **4** (loss of styrene) appeared in the spectrum as a result of an olefin metathesis reaction. Moreover, when either **1** or **2** was mass-selected in the first quadrupole, and then allowed to react with 1-butene in the second octopole, the only metathesis product we obtained in both cases was **4** (Figure 1). Complex **3** exhibited considerably lower reactivity with alkenes in comparable experiments.[9]

With cyclobutene[10] or norbornene, the new complexes **5a** ($n = 1$) and **6** ($n = 1$) were formed predominately. Their masses correspond to the adducts of **2** with the cycloalkenes, as expected for ROM products. Collision-induced dissociation (CID) of **5a** ($n = 1$) or **6** ($n = 1$) led to loss of the cycloalkene mass,[11] presumably reforming **2** (Scheme 2). Closer exami-

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