# Photopatterned Hydrosilylation on Porous Silicon[**]

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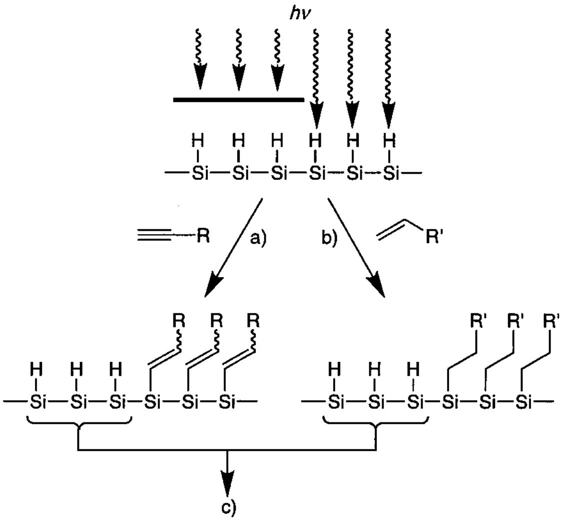
Porous silicon (por-Si) is a material produced by the anisotropic anodic or chemical corrosion of crystalline silicon by hydrofluoric acid.[1] The resulting hydride-passivated surface is populated with Si–H$_x$ bonds ($x = 1, 2, 3$), exposed Si–Si bonds, and defects such as open valence, "dangling" Si atoms.[2] The por-Si material is composed of this surface, sublaminal nanocrystalline Si, and 55–95% empty space.[1] The report of visible photoluminescence (PL) in 1990[3] has attracted interest in the integration[4] of efficient[5] light-emitting por-Si devices into extant and future Si processing for high-speed, optoelectronic systems. We have been developing strategies for improved passivation of the por-Si surface and its effects on PL and chemical stability.

Recent developments in the functionalization of porous silicon have enabled Si–C bonds to be formed on the por-Si surface by attacking the weak Si–Si bonds of exposed nanocrystalline submaterial with Grignard[6] or alkyllithium[7] reagents. Grignard and alkyllithium transmetallation,[8] and the use of Lewis acid catalysis[9] have been used to exploit the large population of surface Si–H bonds. Thermal,[10] radical-mediated,[11] and UV photolytic[12, 13] alkene hydrosilylation is known on flat Si(100) and Si(111) hydride surfaces.

We now report that it is possible to achieve efficient functionalization of the por-Si surface through white light promoted hydrosilylation of unsaturated C–C bonds at 25°C (Scheme 1). The light used for the functionalization is derived from an ordinary tungsten ELH light source of moderate intensity (0.22–44 mW cm$^{-2}$); a neat substrate is added to the surface under an inert atmosphere and the excess washed off after exposure times as short as 15 min. FT-IR transmission spectra of surfaces (Figure 1) prepared through hydrosilylation of 1-dodecene (surface **1**), 1-dodecyne (surface **2**), and styrene (surface **3**) are shown in Figure 2. The degree of incorporation of 1-dodecyne, determined at a constant exposure time (30 min), was dependent upon the light intensity at the sample (Figure 3). Low levels of substitution were observed for control experiments in the absence of light. Photoluminescence is largely retained after functionalization, which is essential for optoelectronic applications. Surfaces **1** and **2** show an average PL intensity of 97 ± 10% and 61% ± 10%,[14] respectively, relative to freshly prepared por-Si samples. A red shift of approximately 10 nm is observed in the maximum PL wavelength of functionalized samples as demonstrated in Figure 4 for surface **1**. Surfaces **1** and **2** are chemically stable to extended treatment (30 min) in boiling aerated, aqueous KOH (pH 10) solution. This is by far the simplest and most economical functionalization and stabilization strategy yet reported.



Scheme 1. White light promoted hydrosilylation on por-Si. By using a mask (black line) to protect part of the surface, the remaining surface can be functionalized with alkynes (a) or alkenes (b) before either dissolution of the unfunctionalized region in alkali or by hydrosilylation with a different substrate (c).

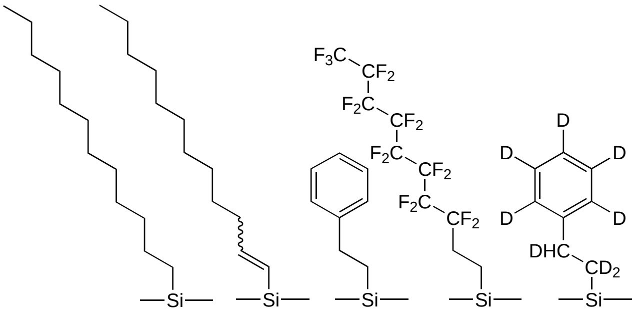


Figure 1. Surfaces prepared through white light promoted hydrosilylation on por-Si.

A very useful regiospecific application of the light-promoted hydrosilylation reaction involves alkyl substitution of the por-Si surface through photopatterning.[15] A white light pattern is focused on a por-Si sample to which neat liquid alkene or alkyne has been applied. After reaction times of 15 min or longer, alkyl incorporation in the illuminated areas can clearly be identified under PL conditions. Functionalized regions appear redshifted relative to nonfunctionalized regions as demonstrated by Figures 5a and 5b for the 1-dodecyne (surface **2**) and 1-dodecene (surface **1**) reacted surfaces, respectively. Photopatterning conducted with simple laboratory apparatus and a reducing lens (f/75) can achieve 40 μm resolution (25.0 lines mm$^{-1}$) between light and dark areas from a focused USAF 1951 resolution target.[16] Si lithography can be accomplished by treatment of the photopatterned sample in a boiling solution of alkaline KOH (pH 12, 15 s),

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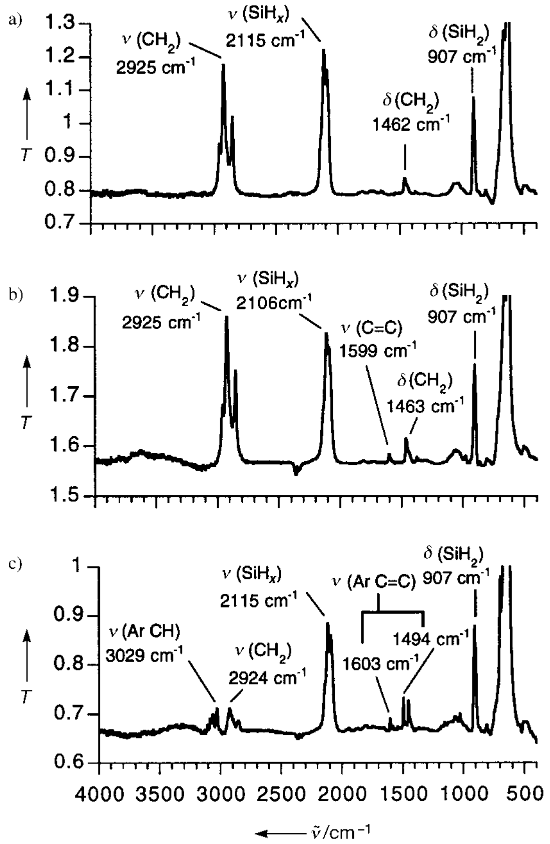

Figure 2. Transmission FT-IR spectra of surfaces **1** (a), **2** (b), and **3** (c), after 60 min at a light intensity of 22 mW cm$^{-2}$, 44 mW cm$^{-2}$, and 44 mW cm$^{-2}$, respectively. $T$ = transmission.

which destroys normal por-Si[17] but leaves functionalized por-Si intact (Figures 5c, d). A por-Si sample was functionalized with two different types of substrates by illuminating half of a wafer while it was treated with neat styrene. After reaction excess styrene was washed off, the entire sample treated with 1-dodecene, and the second half exposed to light. FTIR spectra of the two sides showed almost exclusively phenethyl and dodecyl incorporation, respectively (Figure 6).

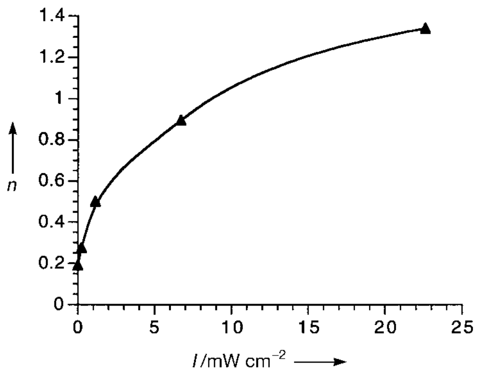

Figure 3. Relationship between incorporation and light intensity $I$ for 1-dodecyne hydrosilylation on por-Si. The peak intensity of the $\nu_{as}(CH_2)$ vibration at 2925 cm$^{-1}$ was used to determine the level of incorporation $n$. Because different samples were prepared for each data point, each was normalized with respect to the $\nu$(Si–H$_x$) peak intensity at 2100 cm$^{-1}$ before the hydrosilylation reaction so that absolute intensities of $\nu_{as}(CH_2)$ could be compared.

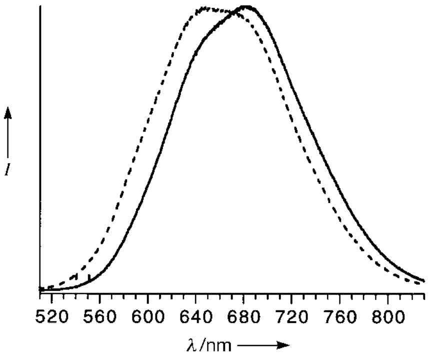

Figure 4. PL spectra of freshly etched por-Si (dotted line), and of por-Si after 60 min hydrosilylation with 1-dodecene and illumination with white light at an intensity of 22 mW cm$^{-2}$ (surface **1**, solid line). $I$ = intensity.

Preliminary mechanistic explorations suggest alkene and alkyne hydrosilylation on the surface of por-Si. By using [D$_8$]styrene as a substrate (surface **5**), a molecule with no C–H bonds, hydrosilylation was observed by the appearance of methylene vibrations at $\tilde{\nu}_{CD-H}$ = 2917 and 2846 cm$^{-1}$ in the IR spectrum,[18] which indicates the transfer of a surface hydride

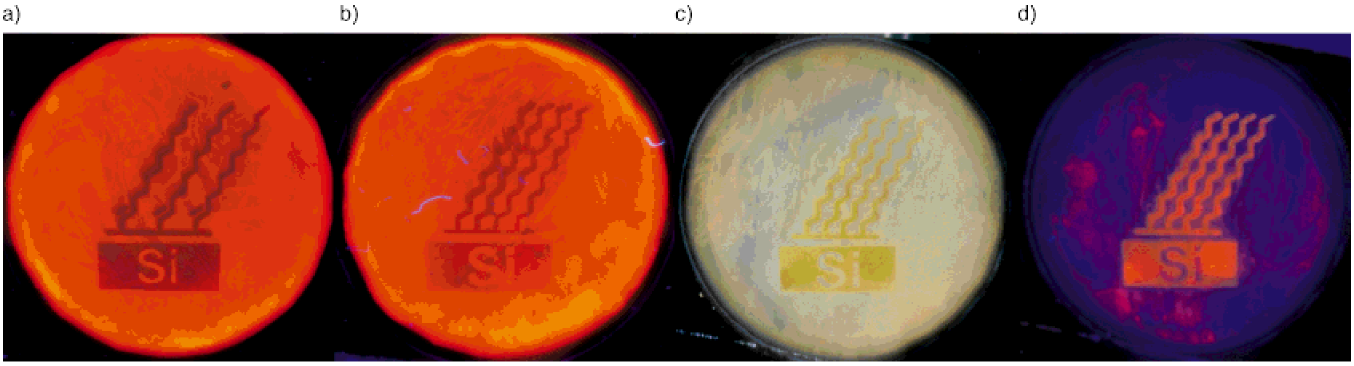

Figure 5. Photographs of por-Si samples (12 mm diameter) prepared through light-promoted hydrosilylation of 1-dodecyne (surface **2**) and 1-dodecene (surface **1**) through masking procedures. (a) The functionalized section of surface **2** appears as the darkened, red-shifted patterned area when illuminated with a 365 nm hand-held UV lamp. The other areas of the wafer are unfunctionalized (native Si–H termination). (b) Surface **1** (redshifted patterned area) upon illumination with 365 nm light. (c) Sample from (b) after boiling in aerated, aqueous KOH solution (pH 12) for 15 seconds. The unfunctionalized porous silicon (grey area) has dissolved, while the hydrosilylated surface (surface **1**, golden area) remains intact. (d) Illumination of the surface from (c) with a 365 nm hand-held UV lamp. The PL of the hydrosilylated area (surface **1**) remains intact while most of the unfunctionalized PL is destroyed.

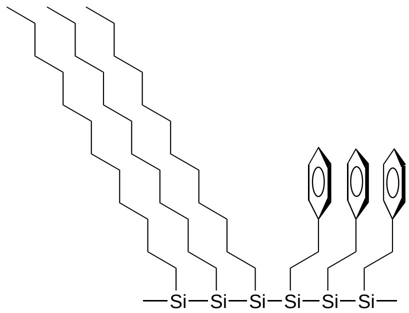

Figure 6. Two halves of a por-Si surface functionalized separately with 1-dodecene and styrene.

to the perdeuterated olefin. Difference transmission FT-IR spectra taken before and after hydrosilylation clearly indicate consumption of the Si–H groups. The role of the white light may be either to generate Si radicals by cleavage of weak Si–H bonds on the surface[13, 19] or to produce photogenerated holes on the surface that are subsequently attacked by alkyne or alkene nucleophiles.[20, 21] The observation that electron-deficient alkynes (phenylacetylene, 4-methylphenylacetylene and 4-chlorophenylacetylene) require longer reaction times (12 h) suggests a mechanism that involves nucleophilic attack. Dangling bonds present on freshly prepared porous silicon can also react with alkenes and alkynes, which accounts for the weak incorporation observed when the hydrosilylation reaction is allowed to proceed in the absence of light.[20] Monochromatic light promoted hydrosilylation of 1-dodecyne at 450, 550, and 650 nm (1 h, $1.8 \times 10^{15}$ photons $cm^{-1}s^{-1}$) showed decreasing substitution with increasing wavelength.[22] The temperature of the silicon wafer during the photochemical reaction, monitored with a thermocouple, showed little change (maximum increase of 2 °C after 1 h at 22 mW $cm^{-2}$), which indicates that thermal activation is not an important factor. The nature of the solvent had no effect on the degree of incorporation as demonstrated by using solutions of 1-dodecyne (20%) in hexanes, toluene, $CH_2Cl_2$, and 0.1 M $N(nBu)_4PF_6$ (in $CH_2Cl_2$).

If functionalized por-Si is to be involved in integratated circuit fabrication, minimal process interference would be advantageous. Photochemical activation of the por-Si surface to effect functionalization is a one-step reaction that avoids the costs and chemical hazards of using highly active organometallic reagents and, as the amount of heating is negligible, observes a minimal thermal budget.[23]

## *Experimental Section*

FT-IR spectra were collected with a Perkin–Elmer 2000 spectrometer in transmission mode, typically at 4 $cm^{-1}$ resolution with 16 to 32 scans collected. Reagents obtained from commercial sources were sparged with argon and filtered over anhydrous alumina in the glove box before use. Light intensities were measured with a hand-held radiometer (Metrologic).

Por-Si material was prepared from polished crystalline silicon wafers (n-type, P-doped, (100), 0.70 Ω cm; Transition Technology International). The etching was carried out in a solution of $HF/H_2O$ (24/24/52) ethanol with either a 0.28 $cm^2$ or 1.1 $cm^2$ area exposed for 3 min at +71.4 mA $cm^{-2}$ (0.28 $cm^2$) or +59.0 mA $cm^{-2}$ (1.1 $cm^2$) and with white light illumination of ~25 mW $cm^{-2}$ from a ELH W bulb (300 W; General Electric). After anodization the samples were washed with ethanol and blown dry under a nitrogen stream.

Hydrosilylation reactions: Typically, a 0.28 $cm^2$ etched wafer, still in the etching cell, was placed into the glove box. The substrate was added (100 µL) to the surface directly, followed if necessary by the solvent (400 µL). A ChemGlass window (borosilicate) was sealed with a Viton O-ring over the etching cell reservoir and clamped. The etching lamp was used as a light source with an intensity of 22.4 mW $cm^{-2}$ at the sample. A thermocouple was assembled with the cell and mounted against the back of the wafer in experiments where the temperature was monitored. In wavelength-dependent studies, a single-grating monochromator (Bausch and Lomb) was used to isolate wavelengths to ~5 nm with transmittance of extraneous wavelengths at approximately $10^{-4}$.

Photoluminescence (steady state) measurements: An Oriel 250 W mercury arc lamp and a Bausch and Lomb monochromator was set to 440 nm with a 450 nm SWP filter (CVI SPF450) as the excitation source, which gave an intensity of 0.2 mW $cm^{-2}$ at the sample. Luminescence was passed through a 490 nm LWP filter (CVI LP490) into an Acton Research Spectra Pro 275 monochromator (0.275 m) and a Princeton Instruments CCD detector (model LN/CCD-1024-E/1) cooled with liquid nitrogen.

Photopatterning: Light from the W etching lamp was passed through a condenser lens onto a mirrored surface and was directed down toward a negative pattern approximately 30 cm from the light source. An achromatic lens (f/75) was positioned about 10 cm below the pattern and about 8 cm above the sample on the laboratory jack. The position of the second lens and the jack surface were manipulated to give the best focused pattern visible on the sample with a magnifying glass. All attempts were made to extinguish nonfocused light from the sample.

1H,1H,2H,2H-Perfluorodecyl terminated surface **4** IR: $\tilde{\nu}_{as}(CH_2) = 2921$, $\tilde{\nu}_s(CH_2) = 2854$, $\tilde{\nu}(SiH_2) = 2114$, $\tilde{\nu}(SiH) = 2082$, $\delta_{as}(CH_2) = 1439$, $\delta_s(CH_2) = 1353$, $\tilde{\nu}_{as}(CF_3) = 1241$, $\tilde{\nu}_{as}(CF_2) = 204$, $\tilde{\nu}_s(CF_2) = 1147$, $\tilde{\nu}(SiO) = 1061$, $\delta_s(SiH_2) = 904$, $\delta(SiH_2) = 657$, $\delta(SiH) = 628\ cm^{-1}$.[24]

$[D_8]$Phenethyl terminated surface **5** IR: $\tilde{\nu}_{as}(CD\text{-}H) = 2917$, $\tilde{\nu}_s(CD\text{-}H) = 2846$, $\tilde{\nu}(ArD) = 2273$, $\tilde{\nu}(CD_2) = 2187$, $\tilde{\nu}(SiH_2) = 2114$, $\tilde{\nu}(SiH) = 2082$, $\tilde{\nu}(Ar\text{-}C{=}C) = 1569$, $\delta_{as}(CD{-}H) = 1450$, $\delta_s(CD{-}H) = 1323$, $\tilde{\nu}(SiO) = 1105$, $\delta_s(SiH_2) = 907$, $\delta(SiH_2) = 661$, $\delta(SiH) = 623\ cm^{-1}$.

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# Cross-Section Molecular Imaging of Supramolecular Microtubes with Contact Atomic Force Microscopy

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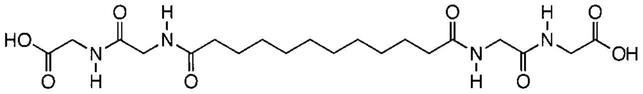
Scanning probe microscopies, especially atomic force microscopy (AFM), are useful methods for obtaining molecularly resolved images of orientation and ordering in organic self-assemblies.[1, 2] In particular, AFM has been used to study two-dimensional, ordered organic molecules adsorbed on well-defined surfaces and at interfaces.[3] While there is an increasing number of studies on AFM imaging of biological macromolecules,[4–6] only a few reports[7–10] have described the morphologies and molecular orientation for synthetic supramolecular assemblies. However, no definitive information on these assemblies, especially along the molecular long axes, has been obtained at molecular resolution by AFM. Meanwhile, supramolecular self-organized fibers and their molecular arrangements have expertly been investigated with scanning and transmission electron microscopy.[11–13] We recently studied hydrogen bond directed self-assembly of chiral fibers[14] and microtubes[10, 15, 16] from synthetic sugar- and peptide-based bolaamphiphiles.[17] In light of the wide applicability of AFM, we explored vertical profiles along the molecular long axes within the microtube[15] made up of glycylglycine bolaamphiphile **1**. Here we report a molecularly resolved layered structure within the tube membranes that was observed by contact AFM in air.



**1**

Figure 1 a shows a nonfiltered AFM image (19 µm × 19 µm) of supramolecular vesicle-encapsulated microtubes made up of **1**. We can observe a clear image similar to that obtained with phase-contrast and dark-field light microscopies (Figure 1 b). Spherical, brighter portions (denoted by arrows in Figure 1 a) correspond to topographically higher regions, and indicate the encapsulation of vesicular assemblies in the compartment.[15] Cross-section analysis of the portions with and without vesicle encapsulation provided information on the thickness of the tube membranes; the value of less than 100 nm corresponds to less than 30–40 molecular layers.[10] In addition, a high-resolution AFM image of the tube surfaces also revealed a distorted hexagonal arrangement of the peptide head groups.[10] These findings indicate that AFM is a very useful tool for studying the molecular packing as well as the morphological dimensions of supramolecular assemblies.

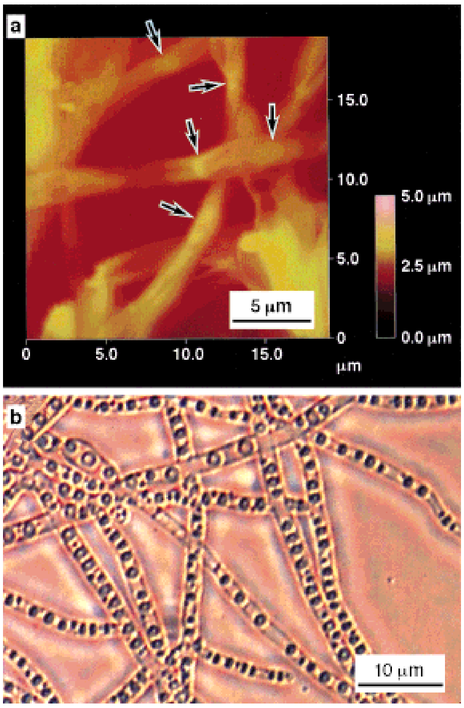


Figure 1. a) AFM height image (19 µm × 19 µm) of vesicle-encapsulated microtubes (denoted by arrows) made up of **1** and b) phase-contrast light micrograph of the microtubes (at 25 °C in water).

The surface morphology of one tube is shown in Figure 2. The AFM image (1.45 µm × 1.45 µm) revealed a crack in the tube membrane. One can see a number of domains arranging like scales of a fish on the top of the tube as well as rodlike

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