

Exciton-Mediated Hydrosilylation on Photoluminescent Nanocrystalline Silicon

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Abstract: A novel white light-promoted reaction using photoluminescent nanocrystalline silicon enables the hydrosilylation of alkenes and alkynes, providing stabilization of the porous silicon without significant loss of the photoemissive qualities of the material. Photopatterning and lithographic fabrication of isolated porous silicon structures are made possible. Experiments and observations are presented which indicate that the light promoted hydrosilylation reaction is unique to photoluminescent silicon, and does not function on nonemissive material. Hydrosilylation using a reactive center generated from a surface-localized exciton is proposed based upon experimental evidence, explaining the photoluminescence requirement. Indirect excitons formed by light absorption mediate the formation of localized electrophilic surface states which are attacked by incoming alkene or alkyne nucleophiles. Supra-band gap charge carriers have sufficient energy to react with nucleophilic alkenes and alkynes, thereupon causing Si–C bond formation, an irreversible event. The light-promoted hydrosilylation reaction is quenched by reagents that quench the light emission from porous silicon, via both charge transfer and energy transfer pathways.

Introduction

Nanoparticles of main group semiconducting compounds (II–VI, III–V, and IV–VI, such as CdSe, InP, and PbS)¹ and elemental materials [group(IV), including silicon and germanium]² have been the focus of intense interest because of their tunable energy gap that is directly related to their size.³ These materials are heavily studied not only to better understand quantum confinement effects,⁴ but for important technological applications, including the development molecular probes in biological systems,⁵ sensing,⁶ and novel device applications.⁷ While syntheses of group(IV) nanoparticles based on silicon and germanium have appeared in the literature,² porous silicon has received by far the most interest because of the ease of synthesis of this material and bright, tunable, room-temperature photoluminescence.⁸ Porous silicon, derived from the same single-crystal Si(100) wafers used in the microelectronics industry, has a complex nanoscale architecture produced via a straightforward electrochemical or chemical etch.⁹ Depending

upon the etching recipe followed, the material contains nanoscale features such as silicon nanoparticles (0-D features) and nanowires (1-D features). Room temperature, visible photoluminescence with efficiencies of 5% can be routinely achieved upon irradiation with UV or blue light.¹⁰ To contrast, the quantum efficiency of bulk silicon photoluminescence is about 6 orders of magnitude lower, $\sim 10^{-5}$ %.¹¹ It is the general consensus in the literature that the intriguing light emission from porous silicon is due to quantum confinement effects of the embedded silicon nanoparticles.¹² Absorption of an incoming photon yields a relatively long-lived exciton (microsecond lifetime);¹¹ radiative recombination of this exciton, as shown in Scheme 1, results in emission of a second photon of lower energy.

In this work, we demonstrate that these excitons are capable of driving a surface hydrosilylation reaction on hydride terminated porous silicon, producing Si–C bonds as shown in Scheme 2.¹³ The excitons are generated through illumination of the surface of photoluminescent porous silicon with white light of moderate intensity (~ 20 mW cm⁻²) for 30–60 min. This reaction is unique as it has no parallels in the known hydrosilylation chemistry of molecular silanes,¹⁴ nor does it function on hydride-terminated flat silicon, which requires

(1) Kamat, P. V. *Prog. Inorg. Chem.* **1997**, *44*, 273. Wise, F. W. *Acc. Chem. Res.* **2000**, *33*, 773.

(2) Nirmal, M.; Brus, L. *Acc. Chem. Res.* **1999**, *32*, 407. Taylor, B. R.; Kauzlarich, S. M.; Delgado, G. R.; Lee, H. W. H. *Chem. Mater.* **1999**, *11*, 2493. Yang, C. S.; Bley, R. A.; Kauzlarich, S. M.; Lee, H. W. H.; Delgado, G. R. *J. Am. Chem. Soc.* **1999**, *121*, 5191. Dhas, N. A.; Raj, C. P.; Gedanken, A. *Chem. Mater.* **1998**, *10*, 3278. Holmes, J. D.; Ziegler, K. J.; Doty, R. D.; Pell, L. E.; Johnston, K. P.; Korgel, B. A. *J. Am. Chem. Soc.* **2001**, *123*, 3743.

(3) Klimov, V. I.; Mikhailovsky, A. A.; Xu, S.; Malko, A.; Hollingsworth, J. A.; Leatherdale, C. A.; Eisler, H. J.; Bawendi, M. G. *Science* **2000**, *290*, 314.

(4) Tomasulo, A.; Ramakrishna, M. V. *J. Chem. Phys.* **1996**, *105*, 3612. (5) Bruchez, M.; Moronne, M.; Gin, P.; Weiss, S.; Alivisatos, A. P. *Science* **1998**, *281*, 2013. Mattoussi, H.; Mauro, J. M.; Goldman, E. R.; Anderson, G. P.; Sundar, V. C.; Mikulec, F. V.; Bawendi, M. G. *J. Am. Chem. Soc.* **2000**, *122*, 12142. Chan, W. C. W.; Nie, S. M. *Science* **1998**, *281*, 2016.

(6) Kim, Y.; Johnson, R. C.; Hupp, J. T. *Nano Lett.* **2001**, *1*, 165.

(7) Yoffe, A. D. *Adv. Phys.* **2001**, *50*, 1. Murray, C. B.; Kagan, C. R.; Bawendi, M. G. *Annu. Rev. Mater. Sci.* **2000**, *30*, 545.

(8) *Properties of Porous Silicon*; Canham, L. T., Ed.; INSPEC: London, 1997. E. J.; Lee, M. J. *Adv. Mater.* **1997**, *9*, 783. *Structural and Optical Properties of Porous Silicon Nanostructures*; Amato, G., Delerue, C., von Bardeleben, H.-J., Eds.; Gordon and Breach: Amsterdam, The Netherlands, 1997.

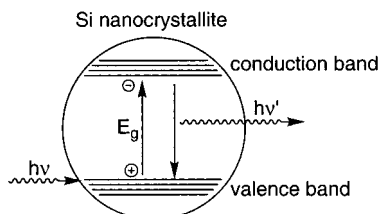
(9) Hérino, R. In *Properties of Porous Silicon*; Canham, L. T., Ed.; INSPEC: London, 1997; p 89. Kelly, M. T.; Chun, K. M.; Bocarsly, A. B. *Appl. Phys. Lett.* **1994**, *64*, 1693.

(10) Canham, L. T. *Appl. Phys. Lett.* **1990**, *57*, 1049. Fauchet, P. M. *J. Lumin.* **1996**, *70*, 294.

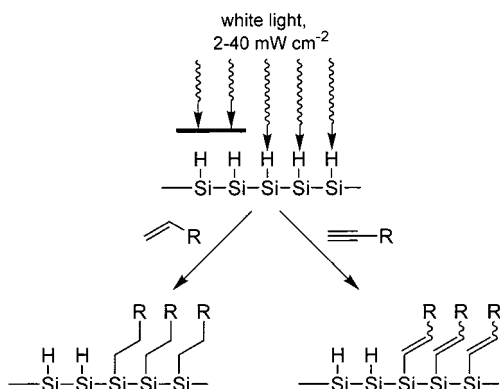
(11) Tsybeskov, L. *MRS Bull.* **1998**, *23*, 33.

(12) Canham, L. T. In *Properties of Porous Silicon*; Canham, L. T., Ed.; INSPEC: London, 1997; p 249. Fauchet, P. M. *Semiconduct. Semimet.* **1998**, *49*, 205.

(13) This work was initially communicated: Stewart, M. P.; Buriak, J. M. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 2357.

Scheme 1. Schematic Representation of a Silicon Nanocrystallite^a

^a Absorption of a photon ($h\nu$) with energy higher than the band gap (E_g) results in promotion of an electron from the valence to the conduction band. Radiative recombination of the exciton results in emission of a photon of lower energy ($h\nu'$).

Scheme 2. Outline of the White Light Mediated Hydrosilylation of Alkenes and Alkynes on Photoluminescent Porous Silicon^a

^a Only illuminated areas react, yielding alkyl and alkenyl terminated surfaces, respectively. Through simple masking procedures, spatially defined areas of different chemical functionalities may be prepared.

substantially higher energy UV illumination and proceeds through an unrelated radical mechanism.^{15–17} In contrast to the vast literature on the redox surface chemistry of nanocrystalline TiO_2 ¹⁸ and other inorganic semiconductors,¹⁹ excitons in silicon nanoparticles have been suggested to drive one only other surface modification reaction, an oxidation reaction of porous silicon in the presence of O_2 .²⁰

While this reaction is intriguing in its own right because it takes place only as a result of the nanoscale size of the silicon nanocrystallites, it serves as a possible route for functionalization of porous silicon surfaces for various applications. Several other very useful and important Si–C bond forming reactions on porous silicon have been described, but all have congeners with molecular or bulk systems.²¹ In addition to possible optoelectronic technologies based on porous silicon,²² several new applications have arisen in which control of surface properties

(14) Brook, M. A. *Silicon in Organic, Organometallic, and Polymer Chemistry*; John Wiley and Sons: New York, 2000.

(15) Cicero, R. L.; Linford, M. R.; Chidsey, C. E. D. *Langmuir* **2000**, *16*, 5688. Terry, J.; Linford, M. R.; Wigren, C.; Cao, R.; Pianetta, P.; Chidsey, C. E. D. *Appl. Phys. Lett.* **1997**, *71*, 1056.

(16) Wojtyk, J. T. C.; Tomietto, M.; Boukherroub, R.; Wayner, D. D. M. *J. Am. Chem. Soc.* **2001**, *123*, 1535. Boukherroub, R.; Morin, S.; Bensebaa, F.; Wayner, D. D. M. *Langmuir* **1999**, *15*, 3831.

(17) Effenberger, F.; Götz, G.; Bidlingmaier, B.; Wezstein, M. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 2462.

(18) Linsebigler, A. L.; Lu, G. Q.; Yates, J. T. *Chem. Rev.* **1995**, *95*, 735. Hoffmann, M. R.; Martin, S. T.; Choi, W. Y.; Bahnemann, D. W. *Chem. Rev.* **1995**, *95*, 69. Hagefeldt, A.; Gratzel, M. *Chem. Rev.* **1995**, *95*, 49.

(19) Kamat, P. V. *Chem. Rev.* **1993**, *93*, 267.

(20) Harper, J.; Sailor, M. J. *Langmuir* **1997**, *13*, 4652

(21) For two recent reviews, see: Buriak, J. M. *Chem. Commun.* **1999**, 1051. Song, J. H.; Sailor, M. J. *Comments Inorg. Chem.* **1999**, *21*, 69.

may be critical.²³ For instance, porous silicon surfaces derivatized with alkyl groups via a Lewis acid mediated hydrosilylation reaction have been shown to be stable in simulated in vivo conditions, thus opening the way for biomedical usages, including biofiltration and in vivo sensing.²⁴ Work from the Sailor group has demonstrated several optical sensing transduction modes from porous silicon for a variety of compounds, including NO, explosives, and biological molecules;²⁵ surface termination has the potential for specific binding and selectivity. Porous silicon also functions as a solid-state matrix for laser desorption mass spectrometry, called desorption ionization on silicon (DIOS).²⁶ Surface derivatization has been shown to play a role in the ionization and recycling potential of these porous silicon chips in the presence of analyte. Surface chemistry is also critical for fundamental studies of light emission and quantum confinement effects in nanocrystalline silicon because surface states play critical roles in exciton localization and quenching (“smart” quantum confinement model).²⁷

Experimental Details

General Methods. FTIR spectra were collected using a Nicolet Nexus 760 spectrometer with a DTGS detector and a nitrogen-purged sample chamber, with 32 scans at 4 cm^{-1} resolution. SEM images were taken with a JEOL JSM-35CF using Au-sputtered samples. Photoluminescence spectra were obtained using 440 nm light from an Oriel Hg arc lamp with a Bausch and Lomb monochromator and 450 nm short-pass filter, giving $0.2\text{--}0.4\text{ mW cm}^{-2}$ at the sample. Photoluminescence emission was filtered by a 490 nm long-pass filter and detected by a Princeton Instruments LN2 cooled CCD with an Acton Research Spectra Pro 275 0.275 m monochromator and fiber optic aperture. SIMS analysis was carried out with a Cameca IMS 4F instrument using a 10 nA 10 kV Cs^+ ion beam, a rastered crater size of $150\text{ }\mu\text{m}$, with a central analysis diameter of $12\text{ }\mu\text{m}$.

Porous Silicon Preparation. Prime-grade 150 mm Si(100) wafers (Silicon Sense) were cleaned before use by soaking and rinsing copiously with ethanol. Detailed guidelines for preparation of porous silicon samples are well described elsewhere.^{28,29} Galvanostatic etching was carried out using 24% HF/26% H_2O /50% ethanol solutions prepared from TraceMetal grade concentrated HF (FisherChemical). A post-etching treatment of rinsing with ethanol and then pentane was used before drying with N_2 and any further handling.³⁰ Alkenes and alkynes were purified before use by passing over anhydrous Al_2O_3 to remove

(22) Pavesi, L.; Dal Negro, L.; Mazzoleni, C.; Franzo, G.; Priolo, F. *Nature* **2000**, *408*, 440.

(23) Stewart, M. P.; Buriak, J. M. *Adv. Mater.* **2000**, *12*, 859

(24) Canham, L. T.; Stewart, M. P.; Buriak, J. M.; Reeves, C. L.; Anderson, M.; Squire, E. K.; Alcock, P.; Snow, P. A. *Phys. Status Solidi A* **2000**, *182*, 521. Canham, L. T.; Reeves, C. L.; Newey, J. P.; Houlton, M. R.; Cox, T. I.; Buriak, J. M.; Stewart, M. P. *Adv. Mater.* **1999**, *11*, 1505. Canham, L. T. *Adv. Mater.* **1995**, *7*, 1033.

(25) Letant, S. E.; Content, S.; Tan, T. T.; Zenhausern, F.; Sailor, M. J. *Sens. Actuators, B: Chem.* **2000**, *69*, 193. Letant, S. E.; Sailor, M. J. *Adv. Mater.* **2001**, *13*, 335. Tinsley-Bown, A. M.; Canham, L. T.; Hollings, M.; Anderson, M. H.; Reeves, C. L.; Cox, T. I.; Nicklin, S.; Squirrel, D. J.; Perkins, E.; Hutchinson, A.; Sailor, M. J.; Wun, A. *Phys. Status Solidi A* **2000**, *182*, 547. Gao, J.; Gao, T.; Sailor, M. J. *Appl. Phys. Lett.* **2000**, *77*, 901. Content, S.; Trogler, W. C.; Sailor, M. J. *Chem. Eur. J.* **2000**, *6*, 2205. Sohn, H.; Letant, S.; Sailor, M. J.; Trogler, W. C. *J. Am. Chem. Soc.* **2000**, *122*, 5399. Janshoff, A.; Dancil, K. P. S.; Steinem, C.; Greiner, D. P.; Lin, V. S. Y.; Gurtner, C.; Motesharei, K.; Sailor, M. J.; Ghadiri, M. R. *J. Am. Chem. Soc.* **1998**, *120*, 12108.

(26) Wei, J.; Buriak, J. M.; Siuzdak, G. *Nature* **1999**, *399*, 243. Shen, Z. X.; Thomas, J. J.; Averbuj, C.; Broo, K. M.; Engelhard, M.; Crowell, J. E.; Finn, M. G.; Siuzdak, G. *Anal. Chem.* **2001**, *73*, 612.

(27) Hamilton, B. *Semicond. Sci. Technol.* **1995**, *10*, 1187.

(28) Halimaoui, A. In *Properties of Porous Silicon*; Canham, L. T., Ed.; INSPEC: London, 1997; pp 12–22.

(29) Lee, E. J.; Bitner, T. W.; Ha, J. S.; Shane, M. J.; Sailor, M. J. *J. Am. Chem. Soc.* **1996**, *118*, 5375.

(30) Bellet, D. In *Properties of Porous Silicon* Canham, L. T., Ed.; INSPEC: London, 1997; pp 38–43.

peroxides (very important!) and by rigorous degassing with argon. A Teflon sample holder, exposing 1.1 cm² of a silicon electrode using ohmic contact with heavy aluminum foil on its unpolished side, was interchangeably used for the etching procedure, light promoted hydrosilylation reaction, and FTIR analysis. Samples described in Table 2 were prepared as follows:

Etching procedure A: n-type (P doped, 0.65–0.95 ohm·cm) silicon was anodized at 7.6 mA cm⁻² for 90 s and then 75.9 mA cm⁻² for 120 s, with full white light illumination (~40 mW cm⁻²). This etching procedure yields a sample with a glassy yellow appearance, showing no macrostructure in cross-sectional SEM. Unless otherwise noted, all samples in this report were prepared according to this procedure.

Etching procedure B: n-type (P doped, 0.65–0.95 ohm·cm) silicon was anodized at 75.9 mA cm⁻² for 180 s, with full illumination. This etching procedure yields a sample with a spongy appearance, and a bilayer structure as determined with SEM that can be removed by indelicate handling. The top layer is microporous, while the bottom layer is macroporous.

Etching procedure C: n⁺-type (Sb doped, 0.008–0.02 ohm·cm) silicon was anodized at 7.6 mA cm⁻² for 90 s and then 75.9 mA cm⁻² for 180 s, with full illumination. This etching procedure yields a sample with a glassy, dark brown colored surface, with no macrostructure seen in cross-sectional SEM.

Etching procedure D: p⁻-type (B doped, 7.5–8.5 ohm·cm) silicon was anodized at 75.9 mA cm⁻² for 120 s, with full illumination. This etching procedure yields a sample with a glassy black surface, which has no macrostructure in cross-sectional SEM.

Etching procedure E: p⁻-type (B doped, 7.5–8.5 ohm·cm) silicon was anodized at 5 mA cm⁻² for 5 min in the dark. This etching procedure yields a sample with a mirror like finish and Fabry-Perot fringes. SEM indicates a layer thickness of 250 nm and a mesoporous structure.

Etching procedure F: n⁺-type (Sb doped, 0.008–0.02 ohm·cm) silicon was anodized at 7.6 mA cm⁻² for 120 s and then 7.6 mA cm⁻² for 240 s in the dark. This etching procedure yields a sample with a glassy yellow colored surface, with no macrostructure seen in cross-sectional SEM.

Etching procedure G: n-type (P doped, 0.65–0.95 ohm·cm) silicon was anodized at 75.9 mA cm⁻² for 6 min, with full backside illumination.³¹ This etching procedure yields a sample with a black glassy appearance.

Light-Promoted Hydrosilylation Reactor. To control for fluctuations in the received light intensity at the sample, as well as angle of incidence and atmospheric contamination, a reactor was constructed for reproducible study of the light-promoted hydrosilylation inside an inert atmosphere glovebox. Light from a tungsten ELH lamp was focused using an RKE eyepiece system (Edmund Scientific), passed through a 400 nm long-pass filter and an IR “hot” mirror (see UV–vis spectra in the Supporting Information), and refocused with an *f*/50 achromatic lens. The measured light intensity at the sample was 20.3 mW cm⁻². Using this system, 0.2 mL of reactant solution is dropped onto the sample, and the sample is then exposed to light. After the desired reaction time (typically 60 min or less), the sample is simply washed with CH₂Cl₂, brought out of the glovebox, and dried gently with a stream of N₂ gas. All reactions were performed at room temperature.

Photopatterning and Lithography. An ELH lamp, a large PCX lens, an acetate transparency photomask, and a *f*/75 mm achromatic lens were used to focus a pattern onto freshly etched porous silicon sample, aligned and focused on a standard lab jack. The photopatterning does not strictly require an inert atmosphere, but if concomitant oxidation of the sample is to be avoided, the process must be carried out either inside a glovebox or using an airtight window. Before illumination, the sample was wetted with just enough alkene or alkyne to thinly coat the surface. Excess liquid resulted in a blurred, poorly resolved pattern. After exposure to light, the samples were simply washed with CH₂Cl₂ or THF, and then gently dried under N₂. If multiple photopatterns were desired, the sample would be wetted, illuminated, rinsed, wetted with the second substrate, illuminated, and so on. The

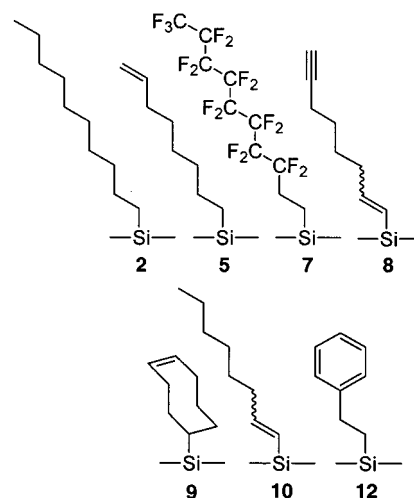


Figure 1. Examples of surfaces produced through the white light promoted hydrosilylation reaction. The numbers underneath each termination correspond with the numerical system used in Table 1.

surfaces were illuminated with the patterns for 5 min each; although longer reaction times would lead to higher incorporation, 5 min is sufficient to stabilize the patterned areas against the alkaline “developing” solution. A KOH solution (unbuffered) was adjusted to pH 12 and brought to a moderate boil in a beaker. A photopatterned sample should typically be dipped for a few seconds in this solution to completely destroy all of the unprotected areas. After removal, the KOH solution is rinsed from the sample by using first ethanol and then CH₂Cl₂ or pentane and then drying using N₂. After this development of the photopattern, the luminescence of the resolved structures can be improved through an additional dip in a 1:1 49% HF (aq)/EtOH solution after the rinsing procedure mentioned above, although it is not essential. Molecules that are able to quench photoluminescence upon physical contact such as phenylacetylene or peroxide-contaminated alkenes cannot be used for photopatterning.

Photolytic Reactions. Photolysis with tris(trimethylsilyl)silane was conducted in a fused quartz ESR tube (Wilmad) that was sealed to prevent air contamination. An equimolar amount of TTMSS (0.05 mL) and 1-pentyne (0.035 mL) were added as titers to the ESR tube with *d*⁶-benzene as a solvent. The tube was either irradiated in a Rayonet reactor with 254 nm light at an intensity of 8 mW cm⁻² or placed in the light-promoted hydrosilylation reactor described above. ¹H NMR (200 MHz) was utilized to analyze the reaction products.

In Situ Light-Promoted Hydrosilylation Quenching. Solutions of the quenchers were prepared in CH₂Cl₂ and added in equal volume to titers of 2.0 M 1-dodecene in CH₂Cl₂. The effective concentration of the quencher was then calculated by using the total volume of the two mixed solutions. The effective concentration of 1-dodecene was always 1.0 M. The quencher/dodecene solutions were premixed before adding to the sample in the light-promoted hydrosilylation reactor. The reaction time in each case was 30 min. The sample was rinsed thoroughly with CH₂Cl₂ after the experiment before removal from the glovebox and FTIR analysis.

Ex Situ Light-Promoted Quenching. A porous silicon sample prepared using etching procedure B was soaked in phenylacetylene for 5 min inside an inert atmosphere glovebox. The sample was then washed thoroughly with CH₂Cl₂ and THF, brought out of the glovebox, and analyzed by FTIR. The same sample was taken back inside the glovebox and reacted with 1-decene in the light-promoted hydrosilylation reactor, and then taken out of the glovebox for FTIR analysis.

Results

The white light-promoted hydrosilylation yields, in a rapid and efficient manner, alkyl- or alkenyl-terminated surfaces for alkenes and alkynes, respectively. Examples of surfaces produced through this method are shown in Figure 1. The reaction is carried out by simply exposing a photoluminescent porous

(31) Lehmann, V. J. *Electrochem. Soc.* **1993**, *140*, 2836.

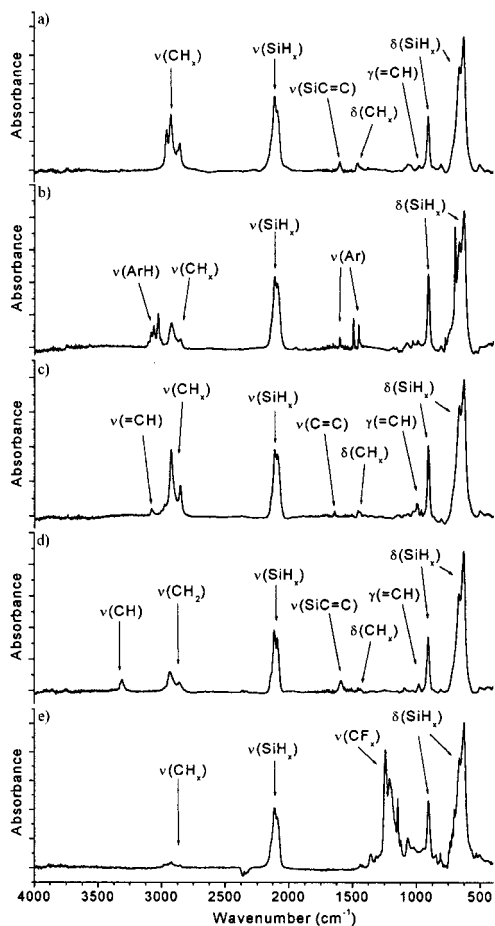


Figure 2. Transmission FTIR spectra of several porous silicon surfaces prepared through etching procedure A using the light-promoted hydrosilylation approach with various substrates: (a) octenyl surface **10**, (b) phenethyl surface **13**, (c) 7-octenyl surface **9**, (d) 7-octynyl surface **8**, and (e) perfluorooctyl surface **4**.

silicon sample to the alkene or alkyne and illuminating it with white light. A wavelength dependence has been observed, with incorporation levels varying as $450 \text{ nm} > 550 \text{ nm} > 650 \text{ nm}$, but because of the simplicity of using a tungsten source, white light was utilized for all experiments here unless stated otherwise.¹³ Monitoring of the surface temperature during the reaction with a thermocouple indicated that the temperature remained below 25°C ; the reaction vessel could also be immersed in a controlled-temperature water bath (20°C) with no difference in reaction coverage. Limiting coverage is usually reached in 3 h, with 90% of the limiting coverage being reached in 1 h or less. Under the best conditions, this reaction consumes less than 20% of the available Si–H bonds of a given sample (vide infra), but this is sufficient to impart considerable chemical stability compared to native porous silicon samples, similar to that of samples stabilized by thermal^{32,33} and Lewis acid mediated hydrosilylations.³⁴ Figure 2 shows FTIR spectra of different surfaces that can be prepared using this simple reaction. The light-promoted hydrosilylation reaction is tolerant of a range of different functionalities, including aryl and perfluoro groups,

reacting primarily and irreversibly with carbon–carbon unsaturated bonds. The chemistry is, however, intolerant of nucleophilic groups such as nitriles and alcohols, resulting in substantial oxidation, possibly due to trace water in these reagents.³⁵

While the chemistry is a hydrosilylation reaction, it has many important differences which differentiate it from superficially similar UV promoted,^{15–17} Lewis acid (EtAlCl_2) mediated,³⁴ and thermally induced hydrosilylation^{32,33} reactions on other hydride terminated silicon surfaces. Importantly, *the reaction only functions on porous silicon samples that are photoluminescent*. To determine the mechanism of the white light-promoted hydrosilylation reaction, analytical FTIR, radical traps, and photoluminescence quenching molecules as probes were utilized. We also demonstrate the utility of this reaction through the fabrication of multipatterned isolated porous silicon structures by photopatterning and lithographic development. Among the many Si–C bond forming reactions known for porous silicon, this is among the easiest, quickest, most economical, and safest to perform.

Stereochemistry and Regiochemistry of the Hydrosilylated Surfaces. Hydrosilylation of alkynes leads to an alkenyl-terminated surface, as indicated by the presence of the $\nu(\text{SiC}=\text{C})$ at $\sim 1600 \text{ cm}^{-1}$. As described in earlier work,^{34,36} this monosilicon-substituted double bond is lowered in energy by at least 40 cm^{-1} when compared to an aliphatic alkene; an identical stretching frequency is noted for molecular vinyl silanes.³⁶ Alkynes yield predominately *trans*-alkenyl surfaces instead of the *cis* stereochemistry seen with both porous silicon³⁴ and molecular trialkylsilanes³⁷ when the reaction is mediated by the Lewis acid, EtAlCl_2 . In Figure 2a, the octenyl surface **10**, the *trans*-olefinic out-of-plane deformation $\gamma(=\text{CH})$ is visible at $\sim 980 \text{ cm}^{-1}$, at approximately the same intensity as the $\nu(\text{SiC}=\text{C})$ peak, which indicates that *trans* alkenes form under these conditions.³⁸ Because such an easily distinguishable marker is lacking for the *cis* alkene, a relative ratio of *cis/trans* products cannot be determined. The silylation tends to occur primarily at the α -carbon of the unsaturated bond, but in some of the surfaces there is evidence of concomitant β -silylation. In the perfluoroalkyl surfaces **4** and **7**, the phenethyl surface **12**, and the 1,7-octadiyne derivatized surface **8** there is a very weak absorbance near 2960 cm^{-1} , most likely the $\nu_{\text{as}}(\text{CH}_3)$ mode possibly resulting from small amounts of β -silylation, although slight surface contamination by physisorbed hydrocarbon cannot be discounted. In the pentenyl surface **6** and octenyl surface **10**, a minor absorbance near 880 cm^{-1} could be due to a vinylidene out-of-plane wag $\omega(=\text{CH}_2)$ resulting from β -silylation of the alkyne.³⁸ Although these assignments are useful only qualitatively, they suggest that there may be some minor variation in regioselectivity for the Si–C bond formation.

Hydrosilylation Efficiency Dependence upon Physical and Chemical Factors. In prior reports, we outlined our analytical method for determining the efficiency of Si–H bond consumption, and therefore surface coverage, by transmission FTIR.^{34,36} The absorbance ratio of the integrated region from 2000 to 2200 cm^{-1} is used, with certain caveats: First, it is assumed that the reaction uses Si–H bonds proportionally to form Si–C bonds. Second, it is assumed that there is little surface degradation from

(32) Bateman, J. E.; Eagling, R. D.; Worall, D. R.; Horrocks, B. R.; Houlton, A. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 2683.

(33) Boukherroub, R.; Morin, S.; Wayner, D. D. M.; Lockwood, D. J. *Phys. Status Solidi A* **2000**, *182*, 117.

(34) Buriak, J. M.; Allen, M. J. *J. Am. Chem. Soc.* **1998**, *120*, 1339. Buriak, J. M.; Stewart, M. J.; Geders, T. W.; Allen, M. J.; Choi, H. C.; Smith, J.; Raftery, M. D.; Canham, L. T. *J. Am. Chem. Soc.* **1999**, *121*, 11491.

(35) Bateman, J. E.; Eagling, R. D.; Horrocks, B. R.; Houlton, A.; Worrall, D. R. *J. Chem. Soc., Chem. Commun.* **1997**, *23*, 2275.

(36) Stewart, M. P.; Robins, E. G.; Geders, T. W.; Allen, M. J.; Choi, H. C.; Buriak, J. M. *Phys. Status Solidi A* **2000**, *182*, 109.

(37) Asao, N.; Sudo, T.; Yamamoto, Y. *J. Org. Chem.* **1996**, *61*, 7654. Sudo, T.; Asao, N.; Gevorgyan, V.; Yamamoto, Y. *J. Org. Chem.* **1999**, *64*, 2494.

(38) Bellamy, L. J. *The Infrared Spectra of Complex Molecules*; Chapman and Hall: London, 1975; pp 50–61.

Table 1. Hydrosilylation Efficiencies for Various Alkenes and Alkynes, on Porous Silicon Prepared with Etch A, Using White Light at 20 mW cm⁻² Light Intensity, for 30 min^a

sample	hydrosilylated molecule	efficiency (% E)
1	1-hexene	16 ± 4
2	1-decene	14 ± 2
3	1-dodecene	13 ± 5
4	1H,1H,2H-perfluorooctene	12 ± 3
5	1,7-octadiene	12 ± 1
6	1-pentyne	11 ± 3
7	1H,1H,2H-perfluorodecene	10 ± 1
8	1,7-octadiyne	9 ± 3
9	1,5-cyclooctadiene	9 ± 4
10	1-octyne	9 ± 1
11	1-dodecyne	8 ± 2
12	styrene	7 ± 4
13	tris(ethylene glycol) methyl vinyl ether	31 (oxidation present)
14	5-hexynenitrile	65 (oxidation present)
15	fullerene, 0.4 M in toluene	<1
16	phenylacetylene	<1
17	4-methylphenylacetylene	<1
18	4-chlorophenylacetylene	<1
19	5-pentynoic acid, 0.9 M in CH ₂ Cl ₂	<1
20	allyloxy(carbonylmethyl)-triphenyl promoted hydrosilylationosponium iodide, 0.83 M in CH ₂ Cl ₂	<1
21	vinylferrocene	<1

^a All samples were delivered as neat liquids unless noted otherwise. Each efficiency value listed here is the average of three runs.

oxidation. Last, it is assumed that the unit absorbance intensities of the Si-H_x bonds are the same and do not change appreciably when adjacent alkyl, alkenyl, or other groups are present. The efficiency, % E, is defined as the ratio between the original integrated intensity of the Si-H_x stretch region A₀ and the amount consumed by a surface treatment (A₀ - A):

$$\% E = (A_0 - A)/A_0$$

Efficiencies are reported here for reactions using the light-promoted hydrosilylation reaction. In Table 1, the reaction was carried out with a variety of alkenes and alkynes using the same etching conditions. In Table 2, the reaction was carried out using different porous silicon samples prepared by varying the etching conditions, the dopant type, and the dopant density (resistivity). The dominant effects on Si-H consumption are related to the side group of the unsaturated bond, namely the steric factors and conjugation of the alkyne. In the case of substrates such as 5-hexynenitrile and tri(ethylene glycol) methyl vinyl ether (surfaces **13** and **14**), concomitant oxidation prevents measurement of an accurate % E, leading to abnormally high values. Varying the concentration of the alkene or alkyne in CH₂Cl₂ did not show a consistent response with respect to light-promoted hydrosilylation efficiency. At high concentrations (4.5–1 M), there was almost no variation of incorporation levels for a given length of time, while at concentrations below 1 M, the observed efficiency decreases rapidly and was highly erratic until near 10⁻⁵ M, the point at which % E is consistently zero. For comparative purposes, use of the Lewis acid mediated hydrosilylation of 1-dodecene proceeded with 28% consumption of Si-H bonds, while with the white light reaction, ~13% of Si-H bonds are replaced. Although there is some difference in the efficiency of the light-promoted hydrosilylation reaction with respect to different doping types and dopant densities, these do not seem to be the overriding factor in determining the success of the light-promoted hydrosilylation reaction; even considerable morphological differences seem to have little effect (see the

Table 2. Hydrosilylation Efficiencies for Various Porous Silicon Samples, with 1-Decene at 20 mW cm⁻² Light Intensity, for 30 min^a

sample appearance	etching procedure	sample doping	resistivity (ohm·cm)	PL ^b	efficiency (% E)
spongy yellow	A	n-type (P)	0.65–0.95	yes	14 ± 3
glassy yellow	B	n-type (P)	0.65–0.95	yes	12 ± 4
glassy brown	C	n ⁺ -type (Sb)	0.008–0.02	yes	9 ± 2
glassy black	D	p ⁻ -type (B)	7.5–8.5	yes	8 ± 4
iridescent	E	p ⁻ -type (B)	7.5–8.5	no	<1
glassy yellow	F	n ⁺ -type (Sb)	0.008–0.02	no	<1
glassy black	G	n-type (P)	0.65–0.95	no	<1

^a Each efficiency value listed here is the average of three runs. The photoluminescent samples emit light at a maximum of λ = 600 to 640 nm. ^b PL = photoluminescence.

Supporting Information). Although the chemical nature of the Si-H bonds is not likely to vary from sample to sample, only samples prepared with specific materials and etching conditions emit light. Photoluminescence remains the sole requirement for light-promoted hydrosilylation reactivity.

Stability Testing of the Hydrosilylated Materials. It has repeatedly been shown that Si surfaces protected by Si-C bonds have considerable resistance to chemical attack when high coverage levels are achieved.^{32–36,39} Such surfaces are capable of surviving a tripartite chemical test, consisting of a CHCl₃ or CH₂Cl₂ degreasing, rinsing with dilute HF, and boiling in basic solution. Physisorbed organics will be removed by the degreasing treatment, oxidized and alkoxy-passivated silicon will be hydrolyzed by the HF, and hydride-passivated silicon will be dissolved by the boiling base. To demonstrate the increased resistance to chemically demanding conditions, a decyl-derivatized porous silicon surface was exposed to boiling alkaline solution at pH 12 and 14 (spectra shown in the Supporting Information). The decyl-terminated sample shows little change after 5, 10, and 30 min at pH 12, with significant oxidation appearing in the form of the ν(Si-O) stretch centered around 1050 cm⁻¹ only at the 30 min mark. At pH 14, unfunctionalized (Si-H terminated) porous silicon is completely corroded in seconds at 100 °C while a decyl-terminated sample, on the other hand, shows corrosion resistance for 5 min, although the ν(Si-O) is becoming the most intense feature.

Photopatterning. A prime advantage of this light-promoted reaction is that its products are spatially localized on the sample according to where the surface is light activated. As the alkenes and alkynes are not significantly reactive toward porous silicon without the surface activation, only the illuminated regions will react, opening possibilities for photopatterning multiple derivatizations on one sample and lithographic formation of structures. Figure 3 shows a sample made in laboratory atmosphere by 3 photopatterning steps, having on it 3 domains of separate derivatization. The spatially localized hydrosilylation of 1-decene, styrene, and 1,5-octadiene results in terminations of decyl, phenethyl, and 4-cyclooctenyl derivatized areas, as demonstrated by FTIR. Following brief exposure (~15 s) to boiling pH 12 KOH, the underivatized areas are destroyed. Irradiation of this surface to 365 nm UV light indicates that the photopatterned areas are still photoluminescent, whereas the unreacted areas are dark. The total time required to prepare this sample was

(39) Examples of organic monolayers on flat silicon demonstrating increased stability: Sieval, A. B.; Demirel, A. L.; Nissink, J. W. M.; Linford, M. R.; van der Maas, J. H.; de Jeu, W. H.; Zuillhof, H.; Sudholter, E. J. R. *Langmuir* **1998**, *14*, 1759–1768. Linford, M. R.; Fenter, P.; Eisenberger, P. M.; Chidsey, C. E. D. *J. Am. Chem. Soc.* **1995**, *117*, 3145–3155. Bansal, A.; Li, X.; Lauermann, I.; Lewis, N. S.; Yi, S. I.; Weinberg, W. H. *J. Am. Chem. Soc.* **1996**, *118*, 7225. Gurtner, C.; Wun, A. W.; Sailor, M. J. *Angew. Chem., Int. Ed.* **1999**, *38*, 1966.

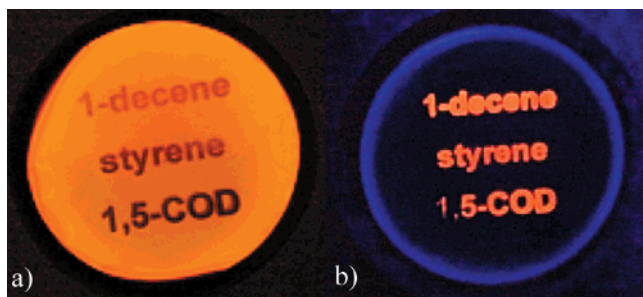


Figure 3. Porous silicon samples (1 cm in diameter), prepared via etching procedure A, photoluminescing under UV (365 nm) irradiation. (a) A triply photopatterned porous silicon structure. The words “1-decene”, “styrene”, and “1,5-COD” are the areas reacted with these same reagents via a masking procedure. The area that spells out “1-decene” is a decyl-functionalized surface; the “styrene” area is a phenethyl surface; the “1,5-COD” area is a cyclooctenyl surface. The reacted areas are slightly red-shifted and darkened as compared to the PL of the unreacted regions of the sample. (b) the same sample after lithographic development using boiling pH 12 KOH solution, showing isolated regions of photoluminescent derivatized porous silicon. The underivatized (Si–H terminated) areas dissolve with the basic treatment and lose photoluminescence while the alkyl-terminated areas are protected, and retain their light emitting properties.

approximately 20 min. The length of illumination time to induce hydrosilylation with each olefin was reduced to 5 min (3×5 min = 15 min), a period that allows enough incorporation to sufficiently protect the surface from hydroxide ion attack.

Photoluminescence Intensity of Derivatized Surfaces.

Previous work on Si–C bond formation has indicated that the nature of the termination has strong effects on the intrinsic photoluminescence of porous silicon.^{40,41} In some cases, however, possible degradation of the surface resulting from the surface chemistry may also be responsible for some of the observed decrease in light emission.⁴² Because of the very gentle nature of this reaction, concomitant surface damage appears to be minimal. Indeed, hydrosilylation of aliphatic olefins such as 1-dodecene shows no decrease in photoluminescence intensity, as shown in Figure 4, only a slight red shift. The effect of vinyl groups, formed from alkyne hydrosilylation, is, however, more dramatic. A surface-bound aliphatic alkenyl group, octenyl, induces ~66% quenching, and hydrosilylation of the conjugated alkyne, phenylacetylene and its derivatives, brings about 100% quenching. Based on literature precedent, it is becoming clear that a surface-bound alkyne or alkene conjugated to an aromatic ring is an extremely effective quenching agent, whereas an isolated phenyl⁴³ or vinyl group is not as deleterious.^{40,41}

Light-Promoted Hydrosilylation Reaction Carried Out in Laboratory Atmosphere. While concomitant oxidation occurs, white light-promoted hydrosilylation can be carried out in air. There is a considerably higher absorbance for the silicon–oxygen stretching modes $\nu(\text{Si–O})$ centered at 1050 cm^{-1} when the reaction is carried out in ambient laboratory conditions, but significant organic incorporation formed via hydrosilylation is observed (spectra shown in the Supporting Information). The partial oxidation of the surface in parallel with the hydrosily-

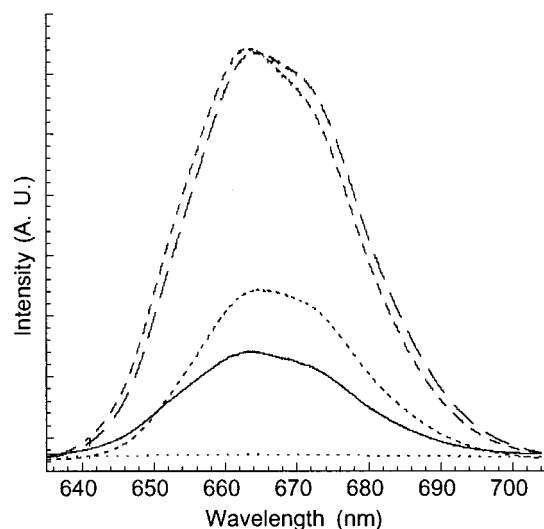


Figure 4. Photoluminescence spectra of various terminations on porous silicon (produced via etching procedure A), in order of decreasing intensity: Si–H (—), dodecyl (---), phenethyl (···), octenyl (— · —).

lation reduces the visible photoluminescence by more than 50% compared to the decyl surface fabricated in inert atmosphere. Surface coverage is much more rapid in the open air light-promoted hydrosilylation reaction, with limiting coverage reached in 30 min or less. The oxidized matter can be removed by rinsing in HF solution but this also removes organic material that may have some oxidation beneath or adjacent to it. The HF rinse also restores some of the lost photoluminescence, but the amount restored varies greatly between samples.

Secondary Ionization Mass Spectrometric (SIMS) Evaluation of Surface Coverage. As shown previously for Lewis acid-mediated hydrosilylation of alkenes and alkynes, SIMS can be used to qualitatively evaluate the continuity of the organic surface coverage extending into the porous layer.³⁴ Because the light-promoted reaction must depend directly upon the penetration depth of white light into the porous layer, SIMS can provide evidence as to whether the reaction takes place only on the top exposed portion of porous silicon or whether it extends more deeply into the material. As shown in Figure 5, SIMS analysis shows that the proportion of carbon with respect to hydrogen, silicon, and fluorine remains relatively constant $1\ \mu\text{m}$ into the material, decreasing slowly after this point.⁴⁴ The penetration depth of blue light into bulk silicon is only $\sim 0.5\ \mu\text{m}$,⁴⁵ but because of the porous nature of the material, the actual penetration depth of the light into porous silicon is presumed to be higher, explaining at least in part the continuous substitution through to $3\ \mu\text{m}$. As compared to the control, an Si–H terminated surface (shown in the Supporting Information), the level of carbon in the hydrosilylated sample is more than 6-fold greater.

Discussion

Here we will propose two mechanisms for the light-promoted hydrosilylation reaction and discuss their agreement with our experimental evidence.

Photolytic Cleavage of Si–H Bonds. There is now considerable precedent in the literature for UV-induced alkene hydrosilylation on hydride-terminated silicon surfaces, starting

(40) Allen, M. J.; Buriak, J. M. *J. Lumin.* **1999**, *80*, 29.

(41) Song, J. H.; Sailor, M. J. *J. Am. Chem. Soc.* **1998**, *120*, 2376. Song, J. H.; Sailor, M. J. *Inorg. Chem.* **1999**, *38*, 1498.

(42) As an example of this, 1-dodecene hydrosilylation through the Lewis acid mediated reaction results in quenching of 80% of photoluminescence, whereas this light reaction results in almost no quenching. Residual aluminum oxide, alkene polymerization products, and other impurities may be responsible.

(43) Kim, N. Y.; Laibinis, P. E. *J. Am. Chem. Soc.* **1998**, *120*, 4516.

(44) The porous layers are thicker than $3\ \mu\text{m}$, but the SIMS analysis was stopped at this point because of the extended periods of time required.

(45) Doan, V. V.; Penner, R. M.; Sailor, M. J. *J. Phys. Chem.* **1993**, *97*, 4505.

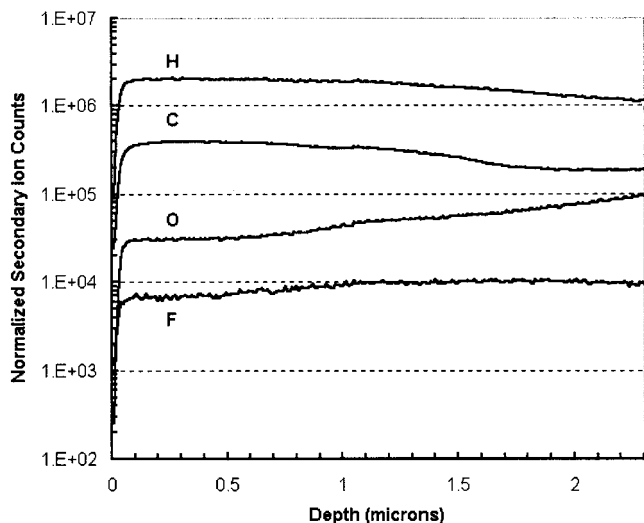
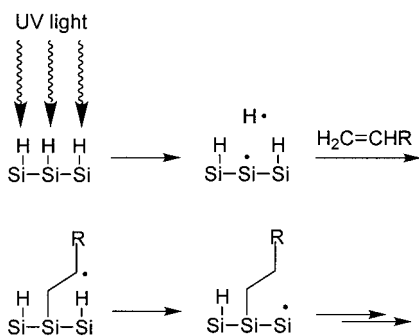


Figure 5. SIMS depth profile of a dodecyl-derivatized porous silicon sample prepared using etching procedure A. The signal levels are normalized to approximately 10^5 counts for Si. The levels of hydrogen and carbon are fairly consistent into the substructure of the sample, at a ratio near $\text{SiC}_3\text{H}_{11}$. The incorporation decreases slightly below $1\ \mu\text{m}$, possibly due to absorption of the higher energy light, although the carbon concentration is six times higher than the unfunctionalized sample at this depth. This shows that light activation penetrates the sample beyond what only blue or UV light could accomplish in bulk solid.

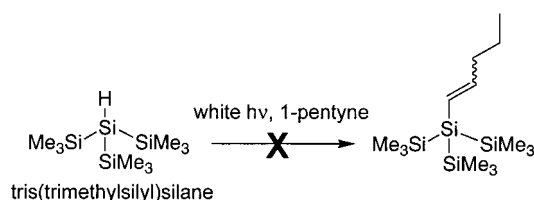
with the work of Chidsey and co-workers.¹⁵ Wavelengths of 350 nm and shorter have been shown to induce rapid (30–60 min) hydrosilylation of alkenes and alkynes on Si(111)–H terminated flat silicon.^{15,16} 380 nm UV light can also induce alkene hydrosilylation on the Si(111)–H surface but reaction times are substantially longer, 24 h, and the reaction is accompanied by a temperature increase to $50\ ^\circ\text{C}$.¹⁷ The proposed mechanism for UV-induced hydrosilylation involves homolysis of a surface Si–H bond, forming a silicon radical (dangling bond).⁴⁶ Because silicon radicals are known to react very rapidly with unsaturated carbon–carbon bonds,⁴⁷ Si–C bond formation is expected to be a facile step, forming the surface bound carbon-based radical on the β -carbon. Abstraction of a neighboring hydrogen completes the hydrosilylation.



Based on the bond strengths of the weakest Si–H bond on a silicon surface, the monohydride/Si–H group ($\sim 3.5\ \text{eV}$), and its reactivity with O_2 , it appears that a minimum of 3.5 eV UV ($\lambda < 350\ \text{nm}$) is required to efficiently perform Si–H bond homolysis.¹⁵ In fact, direct single photon-induced homolysis requires deep UV (157 nm, 7.9 eV), although multiphoton

processes have been observed using near-UV light.^{48,49} The apparent cutoff of Si–H bond homolysis above 350 nm suggests that this radical-based mechanism is not in operation during the white light-promoted hydrosilylation reaction described here, since the shortest wavelength in our system is 400 nm.

To test whether the white light from our ELH element could be used to perform photolytic hydrosilylation, a molecular analogue of the Si–H_x surface was used. Tris(trimethylsilyl)silane (TTMSS), a triply σ -back-bonded silane, was irradiated in the presence of 1-pentyne. The Si–H bond of TTMSS is inductively weakened by its three trimethylsilyl substituents to approximately $79\ \text{kcal mol}^{-1}$, compared to $\sim 90\ \text{kcal mol}^{-1}$ in trialkylsilanes.⁴⁷ After 12 h, no reaction was observed under white light-promoted hydrosilylation reaction conditions at maximum light intensity ($40\ \text{mW cm}^{-2}$). With the same setup, using 254 nm light of a lesser intensity, however, caused almost complete reaction of the TTMSS with 1-pentyne within 2 h, to a multitude of uncharacterized photolysis products.



If a Si–H bond is homolyzed under these conditions to form a silicon radical, by intercepting the silyl radical with an efficient radical trap that itself forms a much less reactive radical molecule, a photolysis-based reaction should be quenched. Toluene solutions of tris(*tert*-butyl)phenol (TBP) and butylated hydroxytoluene (BHT) were used in concentrations up to 2.0 M in the presence of 1-dodecene and 1-dodecyne, without any observable and reproducible quenching effect. Using monodeuterated (OD)-BHT in these experiments did not bring about Si–D bonds on the surface, as was noted in radical-propagated oxidation of porous silicon by DMSO.⁵⁰ Additionally, conjugated alkynes are much less active in the light-promoted hydrosilylation reaction compared with those having alkyl side chains. This reactivity profile is contrary to precedent for silyl radicals in solution chemistry.^{51,52}

On the basis of the insensitivity to the radical traps, the negative control experiment with TTMSS, and the reactivity profile, a radical propagated mechanism can be effectively ruled out. The light from the tungsten-based hydrosilylation reactor is of insufficient energy to photolytically activate Si–H bonds.

Exciton-Mediated Electrophilic–Nucleophilic Attack. Because of the relatively low energy of the white light illumination ($\lambda > 400\ \text{nm}$) and photoluminescence requirement for a successful hydrosilylation, excitons generated in situ are proposed to drive the surface chemistry, as opposed to Si–H homolysis. The excitons form reactive surface states that are a byproduct of room-temperature photoluminescence.

The prevailing model for light emission from porous silicon involves the recombination of a confined, long-lived hole-electron pair in a quantum-confined structure.⁵³ Regions of

(48) Vondrak, T.; Zhu, X. Y. *Phys. Rev. Lett.* **1999**, *82*, 1967.

(49) Pusel, A.; Wetterauer, U.; Hess, P. *Phys. Rev. Lett.* **1998**, *81*, 645.

(50) Song, J. H.; Sailor, M. J. *Inorg. Chem.* **1998**, *37*, 3355.

(51) Kopping, B.; Chatgililoglu, C.; Zehnder, M.; Geise, B. *J. Org. Chem.* **1992**, *57*, 3994.

(52) Chatgililoglu, C.; Ferreri, C.; Gimisis, T. In *The Chemistry of Organic Silicon Compounds*; Rappaport, Z., Apeloig, Y., Eds.; John Wiley and Sons: New York, 1998; Vol. 2, pp 1539–1579.

(53) Cullis, A. G.; Canham, L. T.; Calcott, P. D. J. *J. Appl. Phys.* **1997**, *82*, 909.

(46) Burkhard, C. A.; Kriebel, R. H. *J. Am. Chem. Soc.* **1947**, *69*, 2687.

(47) Kanabus-Kaminska, J. M.; Hawari, J. A.; Griller, D.; Chatgililoglu, C. *J. Am. Chem. Soc.* **1987**, *109*, 5267–5268. Chatgililoglu, C. *Acc. Chem. Res.* **1992**, *25*, 188–194.

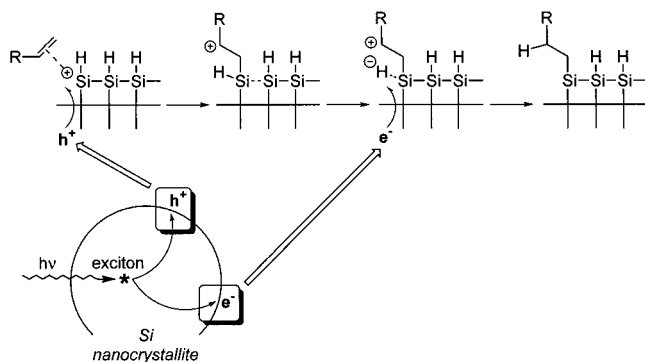


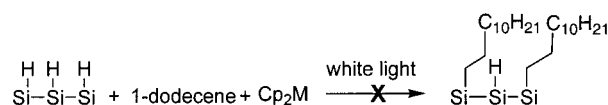
Figure 6. Proposed mechanism for the exciton-mediated hydrosilylation event. An unbound exciton produced by light absorption leads to a surface-localized supra-band gap positive charge. This surface charge can then interact with an alkene and form a silylated β -carbocation upon Si–C bond formation. This carbocation can then abstract a hydride (formally H^+ + electron from exciton) from an adjacent Si–H bond, yielding the neutral organic termination.

crystalline Si whose physical dimensions are less than the mean free path of an electron in bulk Si are able to relax their excited states by emission of light. The pathway to charge recombination is determined by parameters such as the band structure of the material, the lattice spacing, and the availability of traps that may efficiently quench the excited state. The carriers of the photoluminescence are supra-band gap, “hot” electrons and holes, which have a higher relative energy and can be considered more reactive than the distributed charge residues in the space charge layer. In indirect band gap semiconductors such as silicon, the exciton can become uncoupled and allow the hole and the electron to travel separately. The holes and the electrons can localize at mid-gap surface states, which could then become chemically active surface species. For example, excitons generated in nanocrystalline silicon have been proposed as surface-based initiators for solution-phase polymerization of activated olefin monomers.⁵⁴ In addition, exciton involvement has been postulated as one major mode of porous silicon oxidation under 365 or 435 nm light.²⁰ Reduction of an O_2 molecule bound to a surface state on porous silicon with the electron of an electron/hole pair (exciton) yields O_2^- ; this step also results in a net positive charge on the surface as the hole remains within the nanocrystallite. Attack of the positively charged nanocrystallite by the O_2^- leads to oxygen incorporation into the silicon lattice.

In Figure 6, a proposed mechanism for the light-promoted hydrosilylation reaction begins with the formation of a complex between an adsorbed alkene and the surface-localized hole. Attack by an alkene or alkyne nucleophile at an electrophilic silicon center is known in the chemistry of silyl cations in the gas phase.^{55–57} When this reaction is viewed in the silicon nanocrystallite system, there are some slight differences. First, factors contributing to the historic difficulty in isolating a silylium ion,^{58,59} R_3Si^+ , are mitigated in this case. Hyperconjugative donation to the empty orbital, limited somewhat by the size mismatch and electronegativity difference between silicon and carbon in R_3Si^+ , should be much more efficient when the back-bonding substituents are thousands of lattice-locked

silicons. The reaction proceeds directly and irreversibly to form the Si–C bond, resulting in a carbocation stabilized by a β -silyl group.⁶⁰ The high strength and low polarity of the nascent Si–C bond should limit the reversibility of this step. The strongly acidic carbocation can then abstract a hydride from an adjacent hydridic Si–H bond, forming a stronger and less polar C–H bond. This hydride could be formally the product of a hydrogen atom and the electron half of the original exciton e^-/h^+ pair. This hydride abstraction step by a β -silyl carbocation is proposed in mechanisms related to solution-phase hydrosilylation.⁶¹

Reagents which have been shown to quench the light emission of porous silicon⁶² act as energy acceptors^{63–65} or charge acceptors^{20,66} to relax the excited state of the nanocrystallite before radiative recombination can occur. As we have implicated the photoluminescence excited state as an initiator for hydrosilylation reactions, efficient quenching of the light emission should quench the light-promoted hydrosilylation reaction as well.



Solutions of quenchers were dissolved in toluene and used in concentrations from 0.01 to 0.1 M in dichloromethane. Plots of the effect of ferrocene and 9,10-dimethylantracene on the hydrosilylation efficiencies (% E) of 1-dodecene are shown in the Supporting Information. Due to the inherent difficulty in preparing identical samples of porous silicon from one run to the next, there is some variability in the data, but the trend is clear: at concentrations above 0.01 M (Q_{min}), the reaction efficiency drops to below 3%, as opposed to 13% in absence of ferrocene. Table 3 summarizes the effects of photoluminescence quenchers on the hydrosilylation efficiency for the light-promoted hydrosilylation reaction with 1-dodecene at 20 mW cm^{-2} for 30 min in inert atmosphere.

The trend observed in the data shows light-promoted hydrosilylation quenching via exclusive charge transfer, exclusive energy transfer pathways, and with additives that can act as both energy and charge-transfer quenchers. At concentrations below approximately 0.005 M, little hydrosilylation quenching was observed for all additives, except in the cases of vinylferrocene and decamethylruthenocene, which quenched light-promoted hydrosilylation at 10^{-4} M concentrations. The varying degrees of quenching ability do not correlate with the observed rate constants for quenching of light emission in porous silicon. For example, ferrocene is known to quench photoluminescence at diffusion-limited rates, while it is less effective in quenching the light-promoted hydrosilylation reaction than decamethylruthenocene, whose observed quenching rate constant is nearly identical.⁶⁷ This discrepancy may be due to competitive adsorption with respect to the alkene and the quencher. As the observed quenching rate constants are a product of an equilibrium constant for surface physisorption (binding) and an electron transfer rate constant, molecules which can efficiently quench the photolu-

(60) Lambert, J. B. *Tetrahedron* **1990**, *46*, 2677. Lambert, J. B.; Zhao, Y.; Wu, H. *J. Org. Chem.* **1999**, *64*, 2729.

(61) Asao, N.; Yamamoto, Y. *Bull. Chem. Soc. Jpn.* **2000**, *73*, 1071.

(62) Coffey, J. L. *J. Lumin.* **1996**, *70*, 343.

(63) Ko, M. C.; Meyer, G. *Chem. Mater.* **1995**, *7*, 12.

(64) Striplin, D. R.; Wall, C. G.; Erickson, B. W.; Meyer, T. J. *J. Phys. Chem. B* **1998**, *102*, 2383.

(65) Song, J. H.; Sailor, M. J. *J. Am. Chem. Soc.* **1997**, *119*, 7381.

(66) Rehm, J. M.; McLendon, G. L.; Fauchet, P. M. *J. Am. Chem. Soc.* **1996**, *118*, 4490.

(67) Harper, T. H. Ph.D. Thesis, University of California, San Diego, 1998.

(54) Heinrich, J. L.; Lee, A.; Sailor, M. J. *Mater. Res. Soc. Symp. Proc.* **1995**, *358*, 605.

(55) Li, X.; Stone, J. A. *J. Am. Chem. Soc.* **1989**, *111*, 5586.

(56) Chiavarino, B.; Crestoni, M. E.; Fornarini, S. *J. Am. Chem. Soc.* **1998**, *120*, 1523.

(57) Stone, J. A. *Mass Spectrom. Rev.* **1997**, *16*, 25.

(58) Lambert, J. B.; Kania, L.; Zhang, S. *Chem. Rev.* **1995**, *95*, 1191.

(59) For a review, see: Reed, C. A. *Acc. Chem. Res.* **1998**, *31*, 325.

Table 3. In Situ Quenching of Light-Promoted Hydrosilylation Reaction, on Porous Silicon (made via etch A) with 1-Dodecene at 20 mW cm⁻² Light Intensity, for 30 min^a

quencher, [Q]	quenching type	efficiency (% E)	Q _{min} (mol/L)	obsd k _q [Q _{min}] (s ⁻¹)	ref
ruthenocene	charge transfer, energy transfer	3 ± 1	0.01	1.1 × 10 ⁴	67
decamethylruthenocene	charge transfer, energy transfer	<1	0.0001	2.4 × 10 ⁵	67
ferrocene	charge transfer	2 ± 1	0.01	2.8 × 10 ⁷	67
vinylferrocene	charge transfer	<1	0.0001	n.a.	n.a.
ethylferrocene	charge transfer	2 ± 1	0.01	n.a.	n.a.
9,10-diphenylanthracene	energy transfer	4 ± 2	0.01	5.7 × 10 ⁶	65 ^b
9,10-dimethylanthracene	energy transfer	3 ± 1	0.01	3.4 × 10 ⁶	65 ^b

^a Respective values for k_q are from the references cited in the fifth column. Observed k_q[Q_{min}] is the product of the published rate constant and the observed minimum effective concentration of the light-promoted hydrosilylation quenching agent. Each efficiency value listed here is the average of three runs. ^b Refers to the steady-state value.

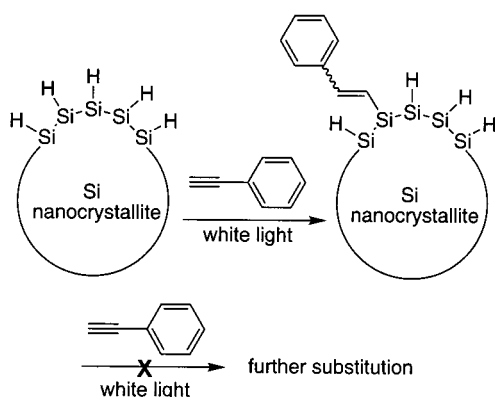


Figure 7. Low incorporation levels are observed when a styrenyl group would be formed through hydrosilylation of phenylacetylene. In the early stages of the reaction, hydrosilylation of a small number of phenylacetylene molecules (here, one is depicted) on a silicon nanocrystallite leads to the styrenyl group, an excellent exciton quencher and site of nonradiative recombination. Further illumination of light does not result in increased incorporation levels because the excitons are efficiently quenched by the styrenyl fragment; the reaction is prevented from progressing any further.

minescence of porous silicon alone may be out-competed for active surface states by the alkene, and vice versa. Indeed, the excellent quenching ability of vinylferrocene is almost certainly due to its reactive vinyl group becoming permanently attached to the porous silicon surface, which would greatly facilitate charge-transfer quenching (vide infra).

If any kinetic insight is to be gleaned from this, it is that the light-promoted hydrosilylation reaction occurs on a slower time scale than the charge-transfer and energy-transfer quenching. It may also be slower, even by orders of magnitude, than the radiative recombination pathway ($\sim 10^5$ s⁻¹),⁶⁷ but the irreversibility of Si-C bond formation may allow the products of even a small reaction cross section to build up.¹⁵ The minimum hydrosilylation quenching concentrations put the effective time scale of the quenchers to within 2 orders of magnitude of the radiative lifetime.

Quenching of the excitation, preventing hydrosilylation, explains the low efficiencies (<1%) when phenylacetylene or vinyl ferrocene is used (see Table 1), due to ex situ quenching. Phenylacetylene, upon hydrosilylation, yields a styrenyl group that is known as a very effective photoluminescence quencher.⁴⁰ During the light-promoted hydrosilylation reaction, reaction of a small number of phenylacetylene molecules, leading to covalently bonded styrenyl groups, may serve to quench the excitons of the nanocrystallite which block any further hydrosilylation, as outlined in Figure 7. Their ability to quench the photoluminescent excited state of the porous silicon halts the reactivity of the sample at low coverage. Similarly, hydrosilylation of an analytically invisible population of vinyl ferrocene

groups during the light-promoted hydrosilylation reaction also prevents further reaction. Even a brief exposure of a freshly etched porous silicon surface to phenylacetylene for 5 min in the dark results in complete removal of the light emission from the porous silicon. This sample shows no light-promoted hydrosilylation reactivity with 1-decene (<1% E) due to the quenched light emission. The Si-H bonds in the sample are still chemically reactive, however, as evidenced by a Lewis acid mediated hydrosilylation carried out on this pretreated sample, with full success (28% E with 1-decene).

Precedent for the reactivity of a silicon-based positive charge in bulk Si can be found in the work of Lewis and co-workers.⁶⁸ Using a ferrocenium hole injector in methanol, methoxy-terminated surfaces could be prepared on flat, single-crystal silicon surfaces, a process postulated to require 2 equiv of ferrocenium oxidant per Si-OMe group formed. Attempts to use ferrocenium to drive hydrosilylation chemistry failed, probably due to the lower energy of this positive charge compared to that of a supra-band gap hole. In addition, it has been shown that Si-C bond formation can take place on porous silicon if a positive bias is applied in the presence of an alkyne (without catalyst or light).⁶⁹

The proposed exciton-mediated surface hydrosilylation reaction explains all the observed reactivity patterns, and justifies the lower incorporation values (% E) as seen using other chemistries, including the Lewis acid-mediated hydrosilylation. The electronic effects on the Si nanocrystallites, along with the physical proportion of photoluminescent nanocrystallites in a particular sample, should determine the observed hydrosilylation efficiencies. If a substantial fraction of a porous silicon layer is not photoluminescent, then efficiencies will be lower since much of the material cannot undergo hydrosilylation via this mechanism.

Conclusions

The white light-promoted hydrosilylation reaction is a novel, unprecedented reaction in silicon chemistry, as it is influenced by quantum size effects as well as Si-H bond reactivity. It is only effective when using porous silicon samples that exhibit strong visible photoluminescence. The hydrosilylation reaction is quenched by charge-transfer and energy-transfer complexes that also are known to quench light emission from porous silicon, but is not affected by radical traps. It is one of the safest and most economical methods of porous silicon functionalization approaches since white light and moderately reactive hydrosilylation substrates are all that are required for this technique. In addition, masking techniques can be utilized to produce

(68) Haber, J. A.; Lauermaun I.; Michalak D.; Vaid T. P.; Lewis, N. S. *J. Phys. Chem. B* **2000**, *104*, 9947.

(69) Robins, E. G.; Stewart, M. P.; Buriak, J. M. *J. Chem. Soc., Chem. Commun.* **1999**, 2479.

regions of differing chemical functionalities. On the basis of reactivity profiles and selective quenching of active surface states, we propose an exciton-mediated mechanism to be responsible for the surface activation. Silicon-centered positive charges are intermediates in this mechanism. This reaction has useful qualities such as the ability to rapidly form chemically stable, free-standing porous silicon structures both in inert atmosphere as well as in air. Further investigation of the photophysical properties of photoluminescent silicon in contact with moderately reactive molecules will shed more light on this interesting new area of silicon chemistry, as well as on the mechanism of the light emission itself.

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Supporting Information Available: FTIR data for all hydrosilylated surfaces, FTIR spectra of the KOH treated dodecyl surface, plan SEM views of porous silicon prepared through etching procedures A and B, SIMS depth profiling of an Si–H terminated surface, energy profile of the filter setup and light source, and quenching profiles of ferrocene and 9,10-dimethylanthracene on the hydrosilylation reaction (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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