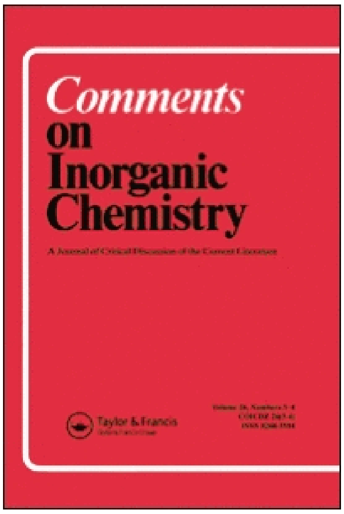

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New Approaches Toward the Formation of Silicon-Carbon Bonds on Porous Silicon

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New Approaches Toward the Formation of Silicon-Carbon Bonds on Porous Silicon

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Porous silicon is a material of intense technological and fundamental interest, due to its high surface area, quantum confinement effects, light emission, and complex nanoscale architecture. There is a strong desire to be able to control the surface properties of this versatile material at will through functionalization with monolayers bound through the stable silicon-carbon bond. Incredibly, the surface chemistry of porous silicon is often very different from that of a silicon-based molecule, or a flat surface, due to interesting electronic effects resulting from both the semiconducting and nanoscale characteristics of the material. Recent results outlining the rapid progress of silicon-carbon bond formation on porous silicon surfaces will be described.

Keywords: porous silicon; photoluminescence (PL); hydrosilylation; nanocrystallites; electrografting; silicon-carbon bonds; excitons; nanotechnology; band gap; high surface area; monolayer

NEW DIRECTIONS FOR THE CHEMISTRY OF SILICON SURFACES IN THE 21ST CENTURY

At the beginning of the 20th century, the science of measurement was at its zenith as the classical view of the universe was just beginning to fray at its edges. Scientists of the day labored to define physical constants to the highest level of precision, exploring the limits of classical theory, and encountering frustrating barriers. Meanwhile, the new field of quantum mechanics was

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being created by the cooperation of many scientists to explain this inherent abstruseness of the world of the very small. Electronic delocalization, discrete energy levels as opposed to continua, and fundamental uncertainty run afoul of the intuitive world we are used to seeing and feeling. Pedagogical simplifications like "particle in a box," "Schrödinger's cat," and GellMann's "eightfold way" have led to a view of quantum mechanics almost as mystical in its ability to confound linear thought.[1]

Such strange phenomena in atoms and molecules, familiar to chemists and physicists, have been studied and reconciled with theories for a long time, but usually have not been implemented in "real world" applications. As we enter the 21st century, however, we find that we are able to make materials with features on the scale of molecules, whose properties are dramatically more diverse than their bulk phase counterparts. Nanoparticles and composite materials using them are finding their way into such everyday applications as automotive plastics[2] and golf clubs.[3] With chemists making ever larger molecules, and engineers making ever smaller materials, a new world has been discovered where physical and electronic properties depend primarily on size. The nanoscale (mesoscale) world, which is now being more actively investigated than ever, is encroaching on the field of applied science as quantum mechanics did with respect to pure science almost 100 years ago.

In the past 25 years, there has probably been no single element whose application has changed the world more than that of silicon. Certainly, the predominance of silicon-based integrated circuit (IC) technology is now so pervasive as to be practically unavoidable in the industrialized world. Since the onset of IC mass production near 1970 (whose growth has been described by Moore's Law),[4] process engineering has enabled a five orders of magnitude increase in circuit density, six orders of magnitude increase in computational throughput, and at least four orders of magnitude increase in energy efficiency.[5] It is now routinely possible to grow perfect single-crystal ingots of silicon that are on the length scale of meters and hundreds of kilograms in weight, refined to 99.9999999% purity. Hundreds of millions of 150 nanometer features can be created simultaneously on polished 300 millimeter wafers with a total surface heterogeneity of less than half of one micrometer (a human hair is about 100 micrometers in diameter). Although these amazing advances in performance and efficiency have been accomplished by engineering the bulk properties of silicon (as well as other aspects of the IC fabrication process), we are fast approaching a new paradigm, wherein simple refinement of existing processes will not provide greater performance.[6]

For example, solid-state transistors are actuated by a switching electrode called a gate. The gate is isolated from the transistor itself by a layer of dielectric (insulating) material. This dielectric is usually silicon oxide but newer, low dielectric constant polymers are coming into use. Due to scaling demands the distance that is covered by this gate oxide, soon to be in the range of 1 nm, will become susceptible to quantum tunneling current, no matter how efficient its dielectric barrier may be.[7] Although 1 nm is an infinitesimal distance in terms of mass fabrication by machines, for synthetic chemists and surface scientists it is actually a fairly convenient distance. Soon, materials performance issues may be dependent on the qualities of an individual or small number of chemical bonds at a surface interface. In molecular chemistry[8] as well as heterogeneous chemistry,[9] charge-transfer interactions at this length scale and shorter are already described by theory and experiment.

Although some of the fundamental knowledge about silicon was discovered long before the solid-state transistor was ever conceived, due to research and development efforts we now know more about its physical and electronic properties in the condensed phase than any element.[10] Now, as progress in miniaturization approaches the physical limits of our current technology, the dominant effects determining device performance are more frequently dependent on molecular and atomic properties of silicon rather than only the bulk properties. A new scheme for fabrication using molecules as components and chemical bonds as wires may arise to complement the current model.[11] The techniques of manipulating silicon at this level will be investigated by organic and inorganic chemists, providing essential guidance in the development of new mesoscale devices.

The majority of the chemically self-assembled surfaces, or self-assembled monolayers (SAMs), that have been studied are made by one of two reaction types: chloro- and alkoxysilanes on silicon oxide,[12] and organothiols on gold, outlined in Figure 1.[13] The reasons for this predominance are related to the simplicity, economy, and reliability of the reactions. People far outside the area of surface chemistry can prepare high-quality surfaces by following a recipe that chemists and engineers have perfected. However, in terms of applications related to efficient charge transport (e.g., molecular wires and the like), there are serious deficiencies presented by these reactions. Organic SAMs from chlorosilanes and alkoxysilanes use glass, an insulator, as a foundation. Monolayers made using the organothiol chemistry are attached by moderately strong[14] (170 kJ mol^{-1}) gold-sulfur bonds, which have the majority of their electron density localized at sulfur. This provides a small degree of current rectification but conductance is limited by the relatively high work function of gold (about 5.1 eV).[15] The gold-thiol SAMs are kinetically labile when subjected to moderate temperatures, chemical attack, or applied potentials.[16] Another less investigated system is alkyl monolayers on silicon.[17] Viewed purely from the perspective of SAMs, monolayers using silicon-carbon bonds would have high strength, moderate polarity, and very low kinetic liability. This stability is hoped to render them tolerant to a wide range of chemical conditions, therefore permitting complex organic synthesis directly on the surface. The interface of the silicon surface could be tailored for a broad spectrum of applications, including bioanalysis, μ-TAS (total automated systems), microelectronics, and others. The potential for a direct, electronically conjugated bonding motif to silicon is also intriguing to interface the many molecular wires and devices that have been synthesized to date.[18]

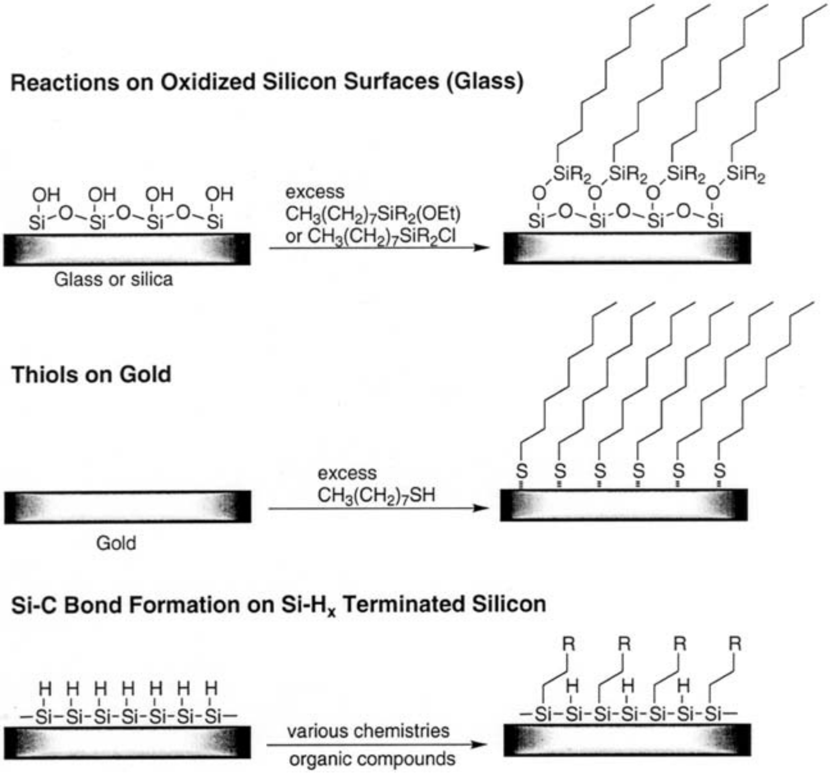


FIGURE 1 Approaches toward the preparation of self-assembed monolayers on glass, silica, gold, and hydride-terminated silicon surfaces. The reaction on glass or silica requires a reactive alkoxy- or chlorosilane, producing Si-O-Si linkages. Thiols on gold spontaneously form thiolates on the gold surface through a chemisorptive process. Various chemistries, discussed here, lead to Si-C bond formation on hydride terminated porous silicon, allowing incorporation of virtually any function group.

In this review, new reactions that efficiently form silicon-carbon bonds on porous silicon surfaces are discussed, along with their attendant benefits to material stability, performance, and versatility. Si-C bond formation on flat silicon surfaces has been recently reviewed.[17]

POROUS SILICON

Porous silicon was first studied by the husband and wife team of Ingeborg and Arthur Uhlir at Bell Labs in the 1950s.[19] They were studying ways of electropolishing clean silicon surfaces using aqueous solutions of HF. They found that, at low current densities, polishing was uneven, sometimes giving colored, spongy material, matte in finish, and definitely not well polished. Their assumption was that the material was a suboxide or oxyfluoride deposit and they did not pursue further investigation. In the 1970s, Japanese workers revealed the porous nature of the material, as well as its true composition (silicon hydride), but were content to use it as a precursor for making high dielectric (low κ) barriers.[20] Although improved photoluminescence (PL) efficiency from porous silicon at 4.2K had been observed in 1984 by Pickering,[21] it was not until a modest report in 1990 by Canham that worldwide attention was drawn to porous silicon.[22] His description of room temperature–visible PL, and proposal that its origins were due to quantum confinement effects, were extremely timely. During the 1980s, the development of efficient light-emitting devices (LEDs) and study of nanoparticles and quantum dots had matured greatly, just in time for a silicon-based model that combined both aspects. Where some people saw an economical way to integrate light-emitting devices into ICs, others saw an easy way to study silicon nanoparticles that were embedded in the material. Within the 10 years following this report, almost 4,000 papers had been published relating to porous and nanocrystalline silicon, compared to less than 200 in all of the years before it.[23] In addition to progress in studying the light emission, completely new applications have emerged for porous silicon, such as biosensing, DIOS mass spectrometry, catalytic growth of carbon nanotubes, and substrates for neuron growth.[24] Due to the myriad of recipes to make porous silicon via electrochemical,[25] chemical (stain etching),[26] or photochemical[27] etching, porous silicon is an easily accessible material for most researchers.

Porous silicon is a high surface area material (hundreds of m^2 per cm^3), made of a silicon skeleton passivated with Si-H_x bonds ($x = 1,2,3$), as shown schematically in Figure 2a.[28] In Figure 2b, the scanning electron micrograph is shown, clearly indicating the high surface area and anisotropic nature of the material. It is different from other high surface area silicon materials such as porous silica, aerogel, or zeolite, because it contains only trace amounts of oxide. This allows some degree of conductance, due to the extensive Si-Si σ-conjugation in the skeleton.[29] However, like silicon hydrides in molecular chemistry, porous silicon is susceptible to oxidation from being handled in air.[30] This oxidation degrades the PL rapidly (timescale of hours), so researchers began looking at ways to improve the stability of the light emission.

Although quantum confinements effects are widely accepted to the basis of porous silicon light emission, the details of mechanism for the PL are still heavily debated, as it is believed to involve multiple pathways.[31] Typical porous silicon samples are able to emit orange-yellow light (700–640 nm or 1.8–2.0 eV) at room temperature as shown in Figure 3 along with the corresponding PL spectrum, which is greater than the bandgap of crystalline

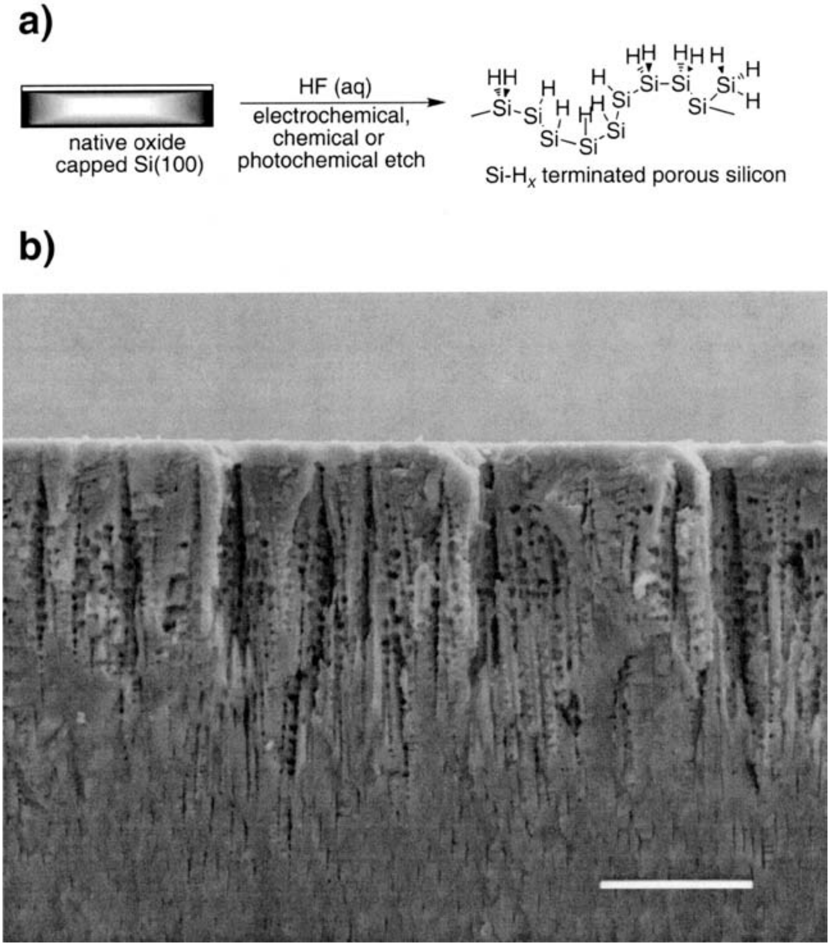


FIGURE 2 a) Schematic of the preparation of hydride terminated porous silicon. The native surface is capped with mono-, di-, and trihydride species to satisfy the tetravalency requirements of silicon. b) Cross-sectional scanning electron micrograph (SEM) of a porous silicon sample, revealing the anisotropic nature of the etch. The bar represents 10 μm.

silicon (1.12 eV). It is even possible, by using variations in the etching procedures, to make samples whose PL is green-blue (~ 2.7 eV).[32] The efficiency of the light emission from porous silicon is ~1%–5%, while from crystalline silicon it is less than $10^{-5}\%$.[33] A hypsochromic shift (blueshift) in the energy gap is a hallmark of quantum confinement effects.[34] Additionally, very highly etched silicon lattice would have many inclusions, bottlenecks, and isolated regions of crystalline silicon. The hydride passivation of the surface is a fair dielectric ($\varepsilon \sim 7$ vs. 4.5 for SiO_2),[35] which enables these isolated regions to trap charged excited states.

If the etching conditions are appropriate to make these isolated regions on the scale of a few nanometers (nanocrystallites), smaller than the mean free path of an electron in silicon,[36] quantum confinement effects become significant. If we consider the form for article in a spherical 3-D box:

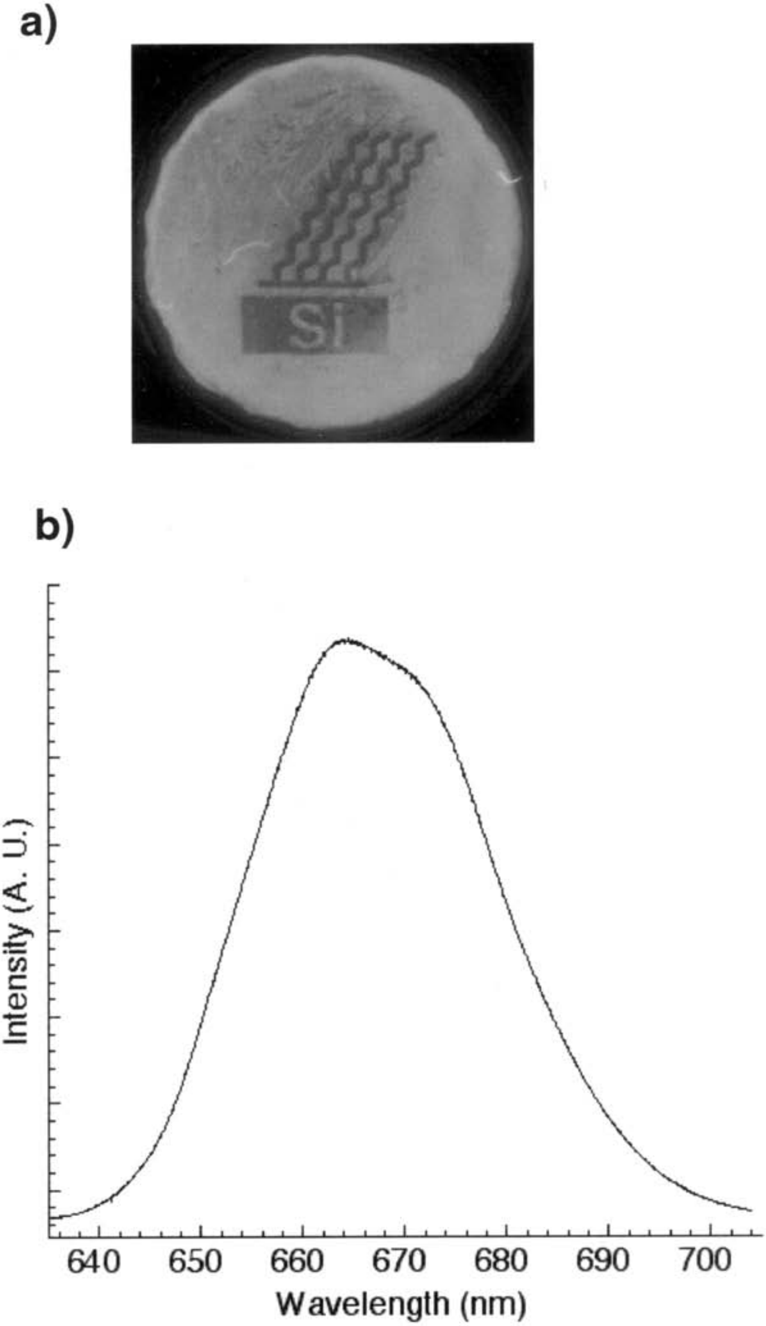
$$E_n = \frac{n^2h^2}{8mr^2}$$

we see that the energy of the confined state increases as the size of the sphere gets smaller. In the specific case of the "quantum dot"[37]

$$E_n = E_g + \frac{n^2h^2}{8mr^2} - \frac{1.8e^2}{\varepsilon r}$$

the overall energy involves a bulk bandgap term, a quantum confinement term, and a coulombic attraction term (which is always very small). For large values of r, the energy converges to E_g, as shown schematically in Figure 4. For small values of r, the bandgap energy is superceded by the quantum confinement term. As shown in Raman spectroscopy and TEM images of photoluminescent porous silicon, the nanocrystallite size is 2–5 nm.[28] Note that it is possible to make highly etched porous silicon samples that have no PL whatsoever. These nanocrystallites, specifically the ones in the 2–5 nm size range, are required for light emission.

The high surface area of porous silicon, as with other nanocrystalline systems, makes the energy gap behavior very sensitive to surface phenomena. This has led to the use of porous silicon as a sensor material for gases, liquids, and biomolecules, where PL modulation upon adsorption and other signal transduction pathways can be used as a quantitative analytical technique.[24,38] However, it also leads to a much greater propensity to oxidize, degrading the PL and other interesting properties by introducing midgap surface states that allow nonradiative relaxation of the excited state (Shockley-Reed-Hall recombination).[39] Although high quality oxide films prepared through rapid thermal oxidation (~ 1000 °C) of porous silicon can actually increase and prolong its PL efficiency,[40] ambient oxidation introduces radicals from Si-Si bond scission, which are highly deleterious to light emission and conductivity.[41] Aspects of the relationship between surface states and chemical bonds at the surface could help in bandgap engineering for


a)
Si
b)
Intensity (A. U.)
640
650
660
670
680
690
700
Wavelength (nm)

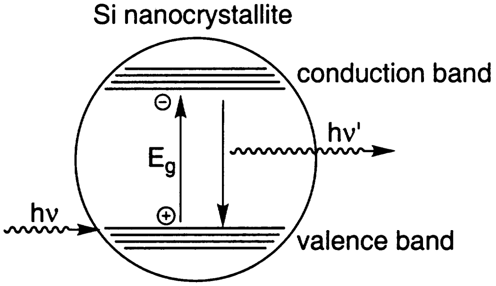


FIGURE 4 Schematic of light emission from a silicon nanocrystallite. An incoming photon (hν) with an energy higher than that of the band gap (E_g) leads to promotion of an electron from the valence to the conduction band. Radiative recombination of this exciton leads to emission of a photon of lower energy (hν′). Reproduced with permission from reference 68b.

nanocrystalline silicon, as well as in the formation of molecular assemblies (molecular wires, recognition elements, etc.) on silicon surfaces in general. We have been exploring new ways of chemically substituting the air-sensitive surface residues with organic functional groups, both to protect the light emission and for fundamental investigation of silicon surface chemistry.

REACTIVE GROUPS ON POROUS SILICON: Si-H_X AND Si-Si BONDS

A freshly etched sample of porous silicon has a native Si-H_x terminated surface with little oxidation. As seen in the transmission FTIR spectrum of Figure 5, the surface is remarkably simple, with only the ν(Si-H_x) stretching vibrations at $\sim 2100\ cm^{-1}$ and the bends, δ(Si-H_x) vibrations around 900 and 600 cm^{-1}. As a result, the porous silicon surface has two chemical handles through which functionalization can be carried out, the Si-H_x and Si-Si bonds. Because the bond strengths and other characteristics of molecular silanes have been extensively studied, they will be discussed to provide insight as to the reactivity of these groups on the porous silicon surface. Unlike hydrocarbons, which are very weakly acidic due to the lower

FIGURE 3 a) Sample of porous silicon (1 cm in diameter) emitting orange light upon irradiation with 365 UV light. The surface has been photopatterned through the chemistry described in Section 5. b) Typical PL spectrum of porous silicon, showing the broad range of wavelengths emitted. The excitation wavelength is 440 nm from Hg arc lamp illumination.

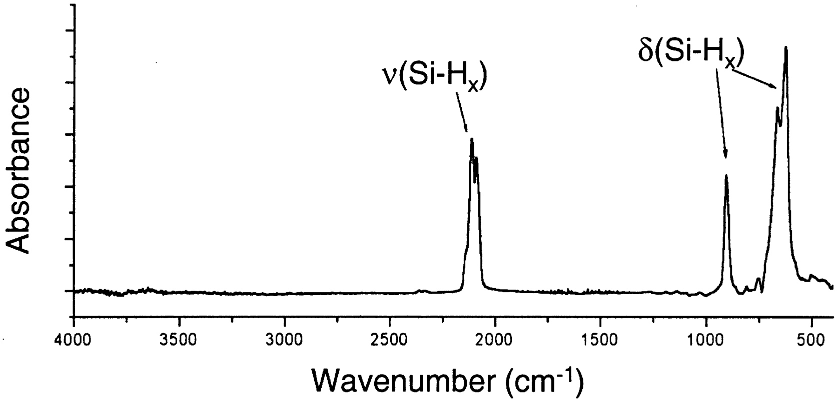


FIGURE 5 Absorbance FTIR for a porous silicon sample. The peak at 2100 cm^{-1} is the Si-H$_x$ stretching peak ν(Si-H$_x$), and the lower energy modes around 800 and 600 cm^{-1} correspond to bends.

electronegativity of silicon versus carbon (1.8 and 2.6 on the Pauling scale), silanes are weakly basic.[42] In Table 1, homolytic bond dissociation energies for silicon and carbon centers are compared.[43] In normal silanes, the Si-H bond is in the same range of strength as a C-H bond. Silyl substituents, however, greatly reduce the strength of Si-H bonds,[44] as is the case in silicon surface Si-H bonds. For surface Si-H$_x$ bonds (assuming the other substituents are silicons), the relative strengths are Si-H$_3$ > Si-H$_2$ > Si-H. This is also the case for Si-Si bonds, which are much weaker in a silicon lattice[45] than in disilane, due to extensive silyl backbonding. Carbon shows a similar effect with respect to carbon backbonding, but to a lesser extent. The difference between lattice Si-Si bonds and that of hexamethyldisilane is greater than 120 kJ mol^{-1}! Silicon molecules and materials are susceptible to oxidation as well, by large thermodynamic and kinetic (autocatalytic)[46] driving forces. Silicon-carbon bonds (1.9 Å) do not show the sensitivity to backbonding substituents that the C-C (1.5 Å) and Si-Si (2.3 Å) bonds do. Moreover, the covalent Si-C bond is stronger than either of the homoatomic bonds, and less reactive than the Si-O or Si-F bonds. The Si-C bond is weakly polarized, with carbon bearing slightly more electron density than silicon. The stability and low polarization of the Si-C bond and its low polarization renders it both thermodynamically and kinetically stable. It is therefore seen by many as the ideal bond through which organic monolayers can be directly linked to the underlying silicon substrate.

Many syntheses for organosilanes have been described in the literature, sufficient to make nearly any functional group attainable.[47] Several of these approaches have been utilized to functionalize porous silicon surfaces, both

TABLE 1 Comparative Bond Strengths for Carbon and Silicon[43]

	Typical bond dissociation energy (kJ mol^{-1})					
Element	-C	-Si	-H	-F	-Cl	-O
C (hydrocarbon)	292–360	370	385–410	480	340	340
Si (silane)	370	270–335	335–376	670	470	540
Si (surface)	370	210	320	670	470	540

flat single crystals and porous silicon. On the other hand, a series of reactions have been published on porous silicon that have no congeners with molecular silane chemistry. In certain cases, the underlying nanostructure can have such a dramatic effect that unique Si-C bond forming reactions can take place. In others, the electronically conductive porous silicon can be used to drive Si-C bond formation, again setting this approach apart from traditional silane chemistry. This report will contrast those functionalizations that are similar to those seen in the molecular literature, summarized in Figure 6, with the

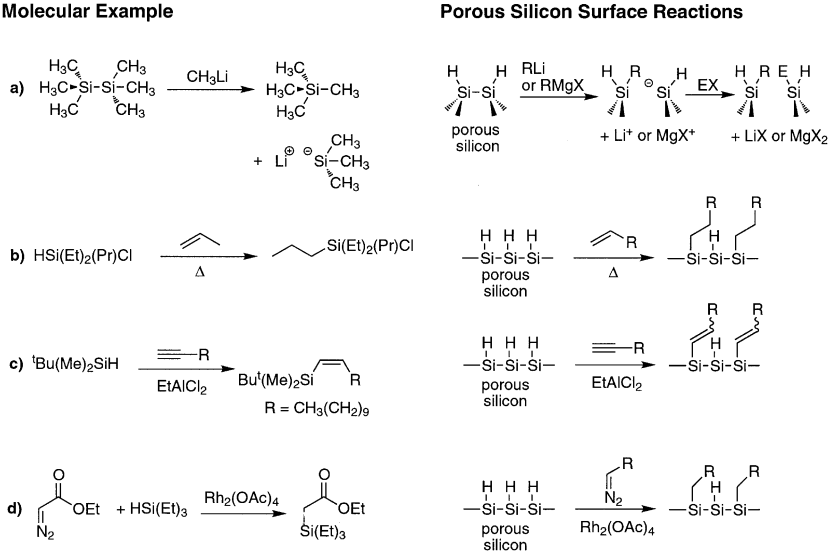


FIGURE 6 Comparison of the four Si-C bond forming reactions carried out on porous silicon that have parallels with the molecular silane literature. A molecular example is given on the left, and the schematic of the reaction on porous silicon is shown on the right. The reactions are cited in the text.

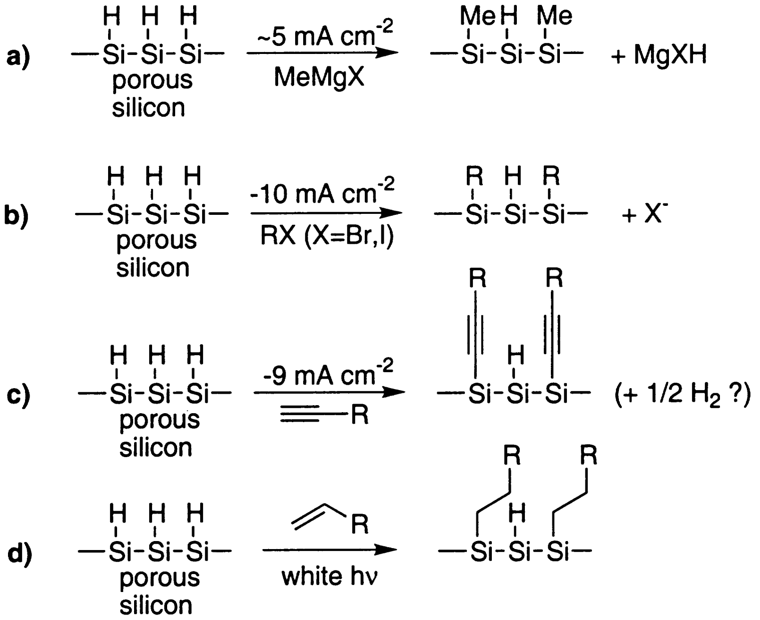


FIGURE 7 Four Si-C bond forming reactions on porous silicon that have no apparent parallels with the molecular silane literature. In these cases, three of the reactions utilize the electrode nature of porous silicon (both anodic and cathodic), and one the stabilized exciton that forms in imbedded nanocrystallites.

growing group of reactions on porous silicon that have no parallels with solution phase silane chemistry, outlined in Figure 7.

ORGANIC MONOLAYER FORMATION ON POROUS SILICON: INSPIRATION FROM THE ORGANOSILANE LITERATURE

Although many different surface terminations were experimented with, most of the initial attempts at protecting the porous silicon surface from oxidative destruction either were controlled oxidation steps or coating the material with a vapor phase thin film agent.[48–51] Although these surfaces are useful in their own right, this overview pertains more specifically to surface reactions that will give organic monolayers, covalently attached through Si-C bonds.

Carbanion Attack

It is known that carbanions from alkyl lithium or Grignard reagents attack disilanes such as hexamethyldisilane, cleaving the Si-Si bond, and resulting in formation of a Si-C bond.[52] Experiments with these reagents showed that organometallic alkylating reagents could form Si-C bonds directly on hydride-terminated porous silicon, as outlined in Figure 6a.[53] Because the nucleophilic attack produces a silyl anion, this provides a chemical handle through which further reactions may be carried out; exposure of the carbanion-treated surface with electrophiles such as acyl chloride result in Si-C(O)CH_3 formation. Examples of surfaces prepared via this method are shown in Figure 8.

Thermal Hydrosilylation

High temperature (T > 150 °C) hydrosilylation of alkenes and alkynes, similar to that performed on hydride-terminated flat crystalline silicon surfaces,[54] has been carried out with porous silicon surfaces by several research groups, as outlined in Figure 6b.[55] These reactions are carried out in a sealed flask or ampoule, completely excluding oxygen or moisture, at or near the reflux temperatures of the long chain organic molecules. The heating times are often quite long, sometimes 16 hours or longer, and preservation of light emission from porous silicon is not clear due to conflicting reports. Examples of surfaces produced through this method are shown in Figure 9. Thermal hydrosilylation with solution phase molecular silanes is known[56] but catalytic reactions are preferred due to the lower temperatures required for the reaction to proceed.[47]

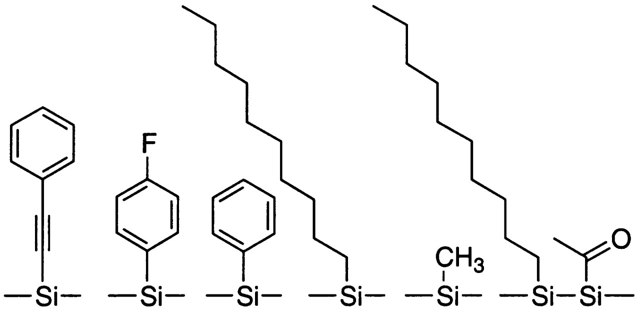


FIGURE 8 Examples of porous silicon surfaces prepared through carbanion attack.

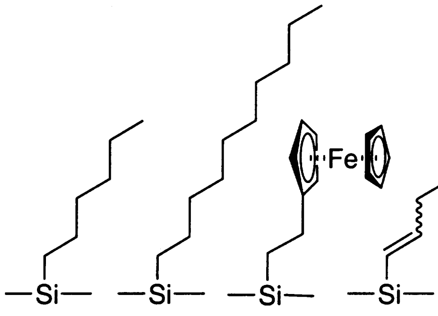


FIGURE 9 Examples of porous silicon surfaces prepared through thermal hydrosilylation.

Metal Mediated Hydrosilylation and Related Reactions

In 1998 it was reported that organically functionalized porous silicon could be prepared via room temperature Lewis acid-mediated hydrosilylation of alkenes and alkynes (Figure 6c).[57,58] Using a Lewis acid catalyst $EtAlCl_2$, previously shown to promote alkene and alkyne hydrosilylation with molecular silanes,[59] porous silicon samples could be very cleanly functionalized with organic groups within an hour (using alkynes) or overnight (using alkenes) at room temperature. This reaction interested many researchers because it was useful for a large variety of hydrosilylation substrates, gave very high chemical stability, caused almost no oxidation, and showed a trend in PL efficiency depending on what kind of molecule was covalently bound to the surface.[60] This reaction permits a rational and systematic approach to covalent porous silicon functionalization reactions to researchers equipped with standard organometallic and inorganic inert atmosphere apparatus, such as Schlenk lines and glove boxes. Examples of surfaces produced via this method are shown in Figure 10. In addition to transmission FTIR characterization, ^{13}C solid state NMR characterization was shown to be a very useful technique.[58] Alkyl- and alkenyl-terminated porous silicon surfaces prepared by this method are stable to extremely chemically demanding conditions such as extended (h timescale) boiling in aerated, aqueous pH 12 solutions, conditions under which hydride terminated porous silicon corrodes in seconds.

Late transition metal compounds have been tested for hydrosilylation and related reactions on porous silicon due to the widespread use of these metal complexes in solution phase, molecular systems.[61,62] Use of $RhCl(PPh_3)_3$ (Wilkinson's catalyst) and a Pt^0-based catalyst, Karstedt's catalyst, led to blackening of the surfaces and loss of all light emission, presumably due to metal reduction and deposition on the surface. Oxidation was also extremely

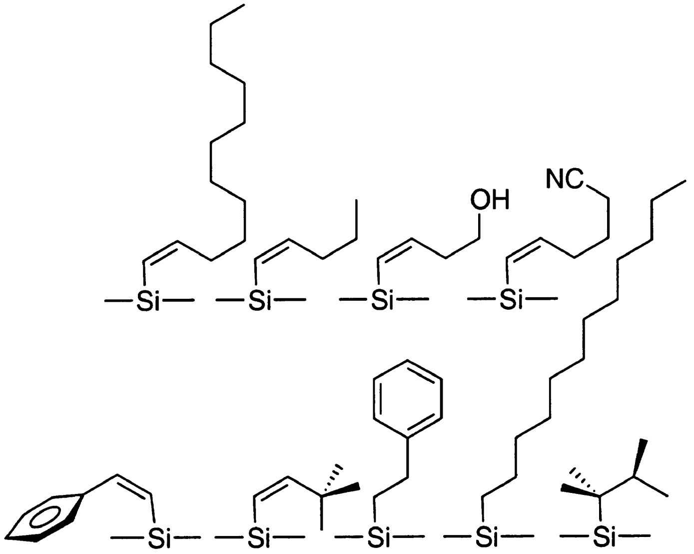


FIGURE 10 Examples of porous silicon surfaces prepared through Lewis acid–mediated hydrosilylation.

difficult to avoid, in spite of considerable precautions. On the other hand, if $Rh_2(OAc)_4$ is used as a catalyst with heating to promote insertion of carbenes from diazo compounds into surface Si-H bonds, little oxidation by transmission IR is observed, which suggests that this method may have synthetic utility (Figure 6d).[62] This reaction is known to function in solution with molecular silanes such as triethylsilane.[63]

ORGANIC MONOLAYER FORMATION ON POROUS SILICON: HARNESSING THE UNIQUE ELECTRONIC PROPERTIES OF THE MATERIAL

Porous silicon is not simply an inert surface that can be approximated by R groups, as in R_3SiH. It is a semiconducting material that can act as an electrode, thus bringing in a whole new pair of reactants into the equation, the electron and the hole. In addition, as will be shown here, unique reactions based upon interesting effects of the nanocrystallites imbedded within the porous silicon matrix can be observed; these reactions have no close relatives with the chemistry of either molecular silanes or flat silicon surfaces.

Electrografting of Carbanions

The first published study of Si-C bond formation on porous silicon in 1996 utilized anodic electrochemical grafting in the presence of methyllithium and methyl Grignard reagents (see Figure 7a).[64] An organic electrolyte in ether permitted transmission of charge between the porous silicon anode and platinum cathode. The anisotropic electric field at the surface of the silicon electrode activates the surface Si-H bonds by creating a local electron deficient surface state. The electron-deficient silicon is especially vulnerable to nucleophilic attack by the methyl anion of the Grignard or alkyl lithium, resulting in Si-C bond formation. Although it is assumed that this reaction liberates HMgBr as a byproduct, it was not characterized. The authors reported a Si-C bond by FTIR evidence, citing the characteristic methyl rocking mode $\rho(SiCH_3)$ near 1260 cm^{-1} and a Si-C stretching mode ν(Si-C) near 775 cm^{-1}. This technique, they later reported, consumed 80% of the available surface sites and is limited by steric hindrance at the surface.[65] Issues relating the surface chemistry to material properties such as PL stability were not systematically addressed.

Electrografting of Alkyl Halides

In a very interesting approach, Sailor and coworkers showed that commercially available and structurally diverse alkyl iodides and bromides can be electrochemically reduced in situ, leading to Si-C bond formation on porous silicon, as shown in Figure 7b.[66] Solutions of the alkyl halide in THF with an organic electrolyte, upon application of a negative bias to the porous silicon electrode, result in Si-C bond formation within 2 minutes. Examples of surfaces prepared through this method are shown in Figure 11. While more work remains to be carried out to fully elucidate the mechanism, reduction of the alkyl halide to the radical and halide anion is probable. Abstraction of a surface hydrogen atom by the alkyl radical will lead to a surface silicon radical (dangling bond). At this point, three possible things could happen: 1) R• could react directly with Si•, forming the Si-C bond, 2) reduction of the Si• with an electron to form Si^- could react in a nucleophilic fashion with RX, leading to Si-R bond formation and release of X^-, or 3) in situ reduction of R• to R^-, the carbanion, which could attack weak Si-Si bonds (*vide supra*).

Electrografting of Alkynes

Work from the Buriak group showed that alkynes can also be grafted to Si-H–terminated porous silicon samples under negative bias (cathodic electrografting, or CEG), as outlined in Figure 7c.[67] An Si-C bond is formed with the terminal carbon of the alkyne, and in contrast to hydrosilylation, the triple bond is not reduced. Examples of surface terminations prepared by this

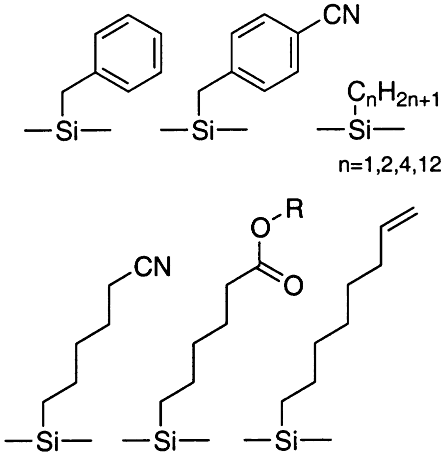


FIGURE 11 Examples of porous silicon surfaces prepared through electrografting of alkyl halides.

method are shown in Figure 12. The alkyne C≡C vibration, upon binding to the surface, can be observed by transmission FTIR at 2179 cm^{-1} for a pentynyl or octynyl dervatized surface. The molecular analog 1-trimethylsilyldodec-1-yne was prepared and its C≡C stretch appears at 2176 cm^{-1}, an almost identical value. In order to definitively prove the alkynyl nature of this vibration, the pentynyl surface was subjected to hydroboration conditions.

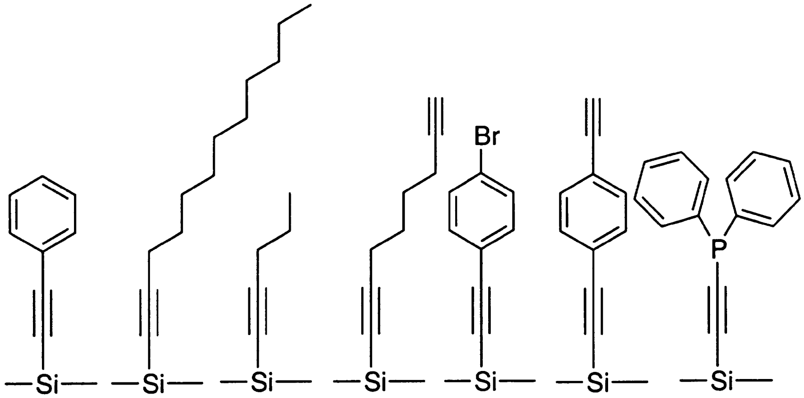


FIGURE 12 Examples of porous silicon surfaces prepared through electrografting of alkynes.

Exposure to disiamylborane, a borane-based reducing agent known to stop at the borylalkene stage, leads to a new stretch at 1580 cm^{-1}, and complete disappearance of the alkyne stretch. The new vibration at 1580 cm^{-1} is of the correct energy to be a silylated, borylated double bond. The molecular equivalent, l-trimethylsilyldodec-1-yne, when hydroborated with the same reagent, has a double bond stretch at 1584 cm^{-1}. These reactivity studies prove that alkynes are grafted to the surface as a triple bond. The cathodic electrografting approach allows for many of the synthesized organic molecular wires to be grafted directly to a silicon device for testing and characterization. The mechanism, while not yet elucidated, may be due to H_2 formation (1/2 of an equivalent) upon reaction of the more electron-rich hydride of a surface Si-H species (due to application of negative bias) with the relatively acidic proton of the alkyne. Alternatively, formation of a surface silyl anion could deprotonate the alkyne, leading to a carbanion that would attack weak and susceptible Si-Si bonds, as is the case with alkyl lithium reagents (*vide supra*).

Positive bias (anodic electrografting, or AEG) was also tried and was found to lead to Si-C bond formation, but with total reduction of the bond order of the alkyne to aliphatic groups as judged by the lack of C≡C and C=C stretching modes in the transmission FTIR.[67] AEG, in contrast to CEG, may be related to a solution phase electrochemical reaction between carbon-carbon unsaturated bonds and silanes, in which the silane is oxidized at the anode to $[R_3SiH]^{+\bullet}$.[68]

Exciton Mediated Hydrosilylation

A very unusual reaction, it was found that simple white light of moderate intensity ($\sim$25–40 mW cm^{-2}) could induce a hydrosilylation reaction on porous silicon surfaces (Figure 7d).[69] Because it has been clearly shown that UV-irradiation with wavelengths shorter than 350 nm are required to induce efficient, room temperature hydrosilylation of alkenes and alkynes on hydride-terminated flat surfaces in a 30–60 minute time frame,[70] a different mechanism was suggested to be in operation. In this white light–promoted hydrosilylation reaction, only wavelengths in the range of 400–600 nm are utilized. It was later found that only photoluminescent porous silicon samples react, pointing to a common set of events linking this hydrosilylation chemistry and light emission.

To explain the relatively low energy of the white light illumination ($\lambda > 400$ nm, intensity 25–40 mW cm^{-2}) and PL requirement for successful hydrosilylation, excitons generated in situ are proposed to drive the surface chemistry, as opposed to Si-H homolysis, seen with UV irradiation and thermal hydrosilylation, as outlined in Figure 13a. The excitons are also responsible for PL in porous silicon,[71] which provides the crucial link between the observed hydrosilylation reactivity and light

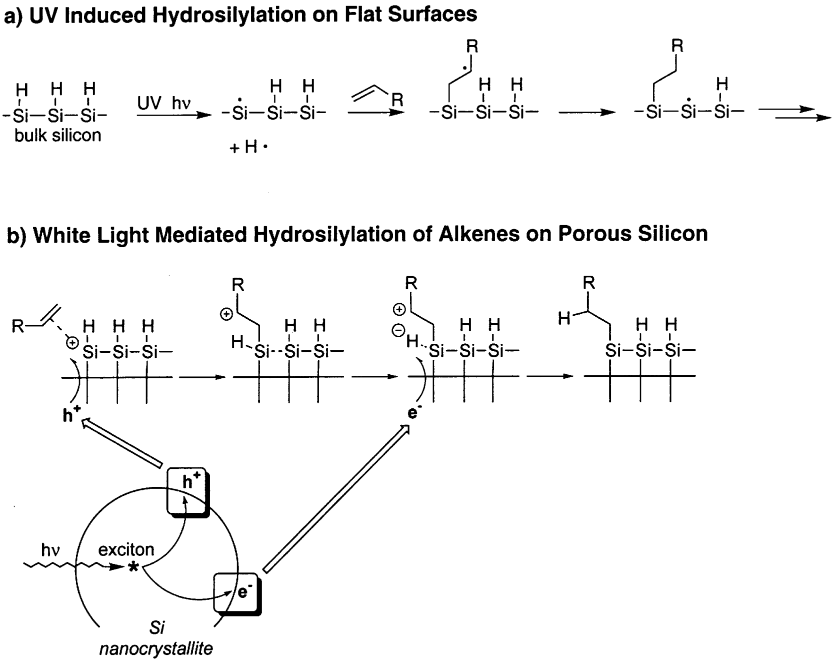


FIGURE 13 The two mechanisms for light-induced hydrosilylation on hydride terminated surfaces. a) Hydrosilylation on flat Si(111)-H surfaces requires UV irradiation with wavelengths shorter than 350 nm in order to carry out the reaction at room temperature in 1 h. The reaction is most likely radical, commencing with homolysis of the Si-H bond. b) Photoluminescent porous silicon samples, on the other hand, can be induced to undergo hydrosilylation with white light of wavelengths longer than 400 nm. The requirement for light emission indicates a link between the excitons formed and the hydrosilylation reaction. In this mechanism, holes on the nanocrystallite surface are attacked by the alkene, forming the Si-C bond. The remaining half of the exciton couple, the electron, can formally combine with a surface hydrogen to produce a hydride, which can react with the carbocation, forming the neutral surface-bound species.

emission. In Figure 13b, 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 proceeds directly and irreversibly to form the Si-C bond, resulting in a carbocation stabilized by a β-silyl group.[72] 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.[73] Experiments with known PL quenching agents such as ferrocene, 9,10-diphenyl-anthracene, and decamethylruthenocene were examined, and were found to prevent white light–promoted hydrosilylation. This work is of special interest because it has no parallels with the chemistry of either bulk silicon surfaces or molecular silanes. The reaction functions only as a result of the nanoscale features of the porous silicon and is tied directly to the PL.

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 14 shows a sample made in laboratory atmosphere by three photopatterning steps, having

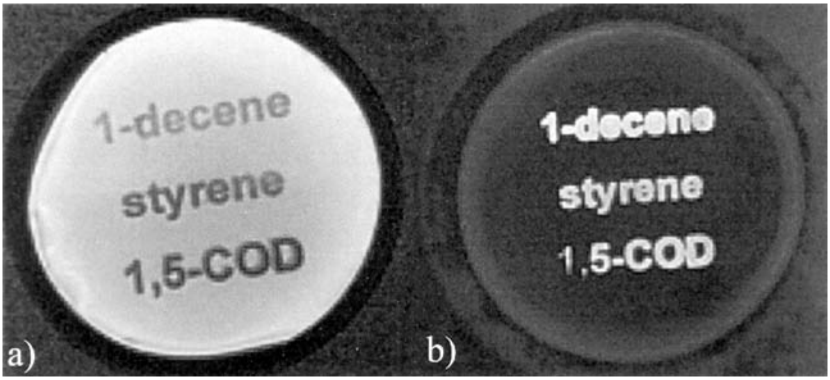


FIGURE 14 1 cm diameter porous silicon samples photoluminescing under UV (365 nm) irradiation. a) A triply photopatterned porous silicon structure. The words "1-decene," "styrene," and "1,5-COD" are the areas reacted with these same reagents via a masking procedure. The area that spells out "1-decene" 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 PL while the alkyl terminated areas are protected, and retain their light-emitting properties. Reproduced with permission from reference 68b.

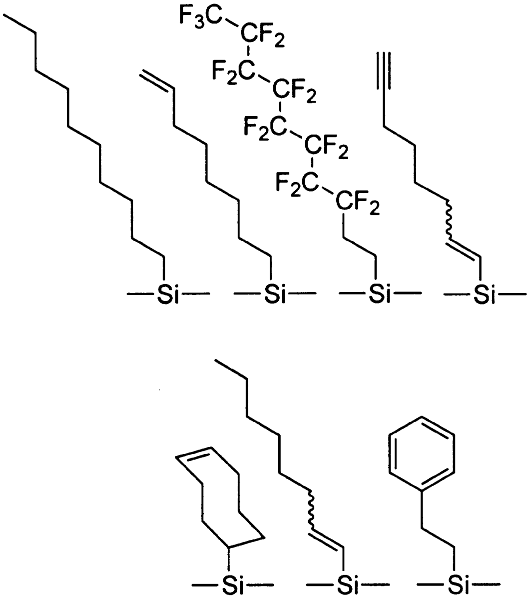


FIGURE 15 Examples of porous silicon surfaces prepared through white light–mediated hydrosilylation.

on it three domains of separate derivatization. The spatially localized hydrosilylation of 1-decene, styrene, and 1,5-octadiene result in terminations of decyl, phenethyl, and 4-cycloctenyl 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 approximately 20 minutes. The length of illumination time to induce hydrosilylation with each olefin was reduced to 5 minutes (3×5 mm = 15 minutes), a period that allows enough incorporation sufficient to protect the surface from hydroxide ion attack. Other examples of surfaces prepared by this method are shown in Figure 15.

CONCLUSIONS

Porous silicon is a superb testing ground for various silicon surface chemistries. For several years, it had been assumed that chemistry known to function with silanes could be applied directly to both hydride-terminated porous and flat surfaces. As the examples indicate, unique electrical behaviors of porous silicon can be harnessed to drive chemistries that have no direct relationship with organometallic molecular silane chemistry. These tantalizing reactivities recently found point to a growing and exciting future for porous silicon chemistry and applications.

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