

# Organometallic chemistry on silicon surfaces: formation of functional monolayers bound through Si–C bonds

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Silicon chips form the backbone of modern computing and yet until recently, the surface chemistry of this technologically essential material has remained relatively unexplored. As the size of devices on silicon wafers shrink (towards gigascale integration), the surface characteristics play increasingly crucial roles in the proper functioning of the device since the ratio of surface atoms/bulk escalates. While surface oxide has served thus far as the main passivation route, there is strong interest in precisely tailoring the interface properties, not only for microelectronics, but other applications including sensors, MEMS and biologically active surfaces. As a result, organometallic and organic chemistry has become essential for the synthesis of functional, modifiable monolayers, bound to non-oxidized silicon surfaces through silicon–carbon bonds. The latest approaches towards preparation of monolayers through Si–C bonds on both flat and photoluminescent porous silicon are described. Wet chemical techniques, accessible to most organometallic/organic chemists are highlighted, but recent developments using UHV conditions also receive attention.

## Introduction

Silicon is clearly the most technologically important material utilized today owing to its ubiquitous role in microelectronic computing. With few exceptions, all microprocessor chips in electronic products are based upon flat, crystalline silicon wafers. In spite of several decades of intense research into the properties and potential applications of silicon, the surface chemistry of this material has only recently begun to be investigated in a systematic fashion.<sup>1</sup> As electronic devices on silicon become progressively smaller, the fraction of atoms residing on or near the surface becomes significant.<sup>2</sup> The chemical nature of these interface atoms thus plays a crucial role in the proper functioning and characteristics of the device. While native oxide on silicon has proven extremely useful in electronically passivating bulk silicon, much attention is being directed towards the synthesis of organic monolayers which can be modified upon demand for specific requirements. By tapping

into the vast resources of organic and organometallic chemistry, a wide variety of functionalities can be synthesized and incorporated which will allow for fine tailoring of surface characteristics for a broad range of applications, some of which are outlined in this review. Because the surface chemistry of non-oxidized silicon is still in its infancy, several different approaches have been taken to first understand its reactivity, and then to subsequently exploit the reactivity to prepare stable, sophisticated interfaces. This review will focus exclusively on the chemistry involving formation of organic monolayers on both flat and porous silicon surfaces bound directly to the underlying bulk material through silicon–carbon bonds, some examples of which are shown in Fig. 1. Wet bench-top reactions are emphasized although recent advances utilizing ultra-high vacuum (UHV) conditions will be outlined. Capping of silica and glass surfaces with alkyl-, alkoxy- and chloro-silanes has been reviewed elsewhere.<sup>3</sup>

## Flat, single crystal silicon

Single crystal silicon wafers of high purity are commercially available and relatively inexpensive due to their wide use in microelectronic applications. The most common surface orientations are Si(111) and Si(100) (*vide infra*) although other Si(*hkl*) orientations are known.<sup>1</sup> Upon exposure to air, single crystal silicon becomes rapidly coated with a thin, native oxide that can be removed chemically with fluoride ion or thermally under UHV conditions. Depending upon the desired electronic properties, silicon wafers are doped in a controlled fashion with electron donating (P, As, Sb: *n*-type) or withdrawing (B: *p*-type) impurities to render the intrinsic material more highly conducting.

## Porous silicon

While much of the effort towards preparation of organic monolayers on silicon has been directed towards flat, single crystal surfaces, a substantial body of research has been dedicated to porous silicon functionalization.<sup>2</sup> Porous silicon is a potentially revolutionary variant of crystalline silicon<sup>4</sup> because of its tunable electro-, photo- and chemo-luminescent properties.<sup>5</sup> While bulk silicon is an extremely poor light emitter, porous silicon can achieve quantum efficiencies in excess of 10%, rendering it technologically important for optoelectronic applications, that is, incorporation of both optical and electronic elements into integrated circuits.<sup>6</sup> Because it is easily prepared through simple galvanostatic,<sup>7</sup> chemical (stain),<sup>8</sup> or photochemical<sup>9</sup> etches from silicon wafers ('bucket' chemistry),<sup>5</sup> porous silicon could be readily integrated with existing silicon-based integrated circuit (IC) manufacturing processes. Other non-silicon-based light emitting materials such as GaAs or organic light emitting compounds will require

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extensive modification of the IC processes for their incorporation into silicon-based chips.

Porous silicon has a highly complex nanoscale architecture made up of one-dimensional crystalline nanowires and zero-dimensional nanocrystallites as demonstrated in Fig. 2. This material has elicited publication of over 4000 papers<sup>10</sup> since the discovery of its photoluminescence in 1990 which is testament not only to its technological potential, but to the fundamental interest in understanding the luminescence phenomena of nanocrystalline particles.<sup>11</sup> The major barrier preventing commercial applications of porous silicon is the instability of its native interface, a metastable Si–H termination (*vide infra*), and thus surface chemistry has proven to be a crucial element for the technological success of this material. The photoluminescence of porous silicon depends strongly upon the surface passivation, with certain functionalities (*i.e.* halogens)<sup>12</sup> resulting in complete quenching of light emission. While highly debated in the literature, it is generally accepted that quantum confinement effects, arising from recombination of entrapped electron-hole pairs (excitons) within the boundaries of nanocrystallites/nanowires with diameters of *ca.* 2 nm, are responsible.<sup>2,5</sup> Surface states associated with various interface species can have dramatic quenching effects if they provide sites for non-radiative recombination of the excitons.<sup>13</sup> The precision of organic chemistry promises to allow for fine tuning of these important interfacial effects, leading ultimately towards an understanding of the role of surface states on semiconducting nanoparticles in general. The nature of the surface bond, sterics, conjugation, and electronics of organic substituents can all be modulated at will and should provide: (i) stable porous silicon surfaces, (ii) modifiable surface characteristics, and (iii) potential to interface with organic conductor/semiconductors/LEDs and biologically relevant molecules for an array of applications.

### Wet chemical functionalization strategies

For the preparation of functionalized, non-oxidized silicon interfaces, silicon–hydride terminated surfaces generally serve as an ideal starting point (Fig. 3). Si–H passivation is only metastable with respect to oxidation under ambient conditions, thus precluding long-term use in most cases. These surfaces can, however, be handled in air for tens of minutes with little degradation which renders them accessible to chemists and materials scientists wishing to use standard Schlenk and glove box techniques.<sup>14</sup> Silicon–hydride termination of commercial,

native oxide capped flat crystal silicon wafers is carried out quickly and efficiently in under 10 min using commercially available fluoride sources. Dilute (1–2%) aqueous HF treatment of a Si(100) wafer yields the (100) dihydride =SiH<sub>2</sub> capped surface, and 40% aqueous NH<sub>4</sub>F of a Si(111) wafer provides the atomically flat (111) monohydride ≡SiH terminated surface.<sup>15</sup> Porous silicon, when etched through standard procedures involving HF, is also hydride terminated but is coated with –SiH<sub>3</sub>, =SiH<sub>2</sub>, ≡SiH groups in a variety of different local orientations and environments owing to the porous nature of the material.<sup>16</sup> All the freshly etched silicon hydride terminated surfaces are chemically homogeneous (>99% H termination) which is essential for clean reactions.

The hydride terminated surfaces are extremely useful surface precursors because the Si–H and Si–Si bonds can serve as chemical handles through which functionalization can be mediated. The body of literature involving functionalization of soluble, molecular silicon–hydride and silicon–silicon containing compounds is vast.<sup>17</sup> Several of these reactions for molecular compounds have been adapted and applied to surfaces, as described here. Other reactions, on the other hand, have no molecular equivalents since they utilize the underlying bulk electronic properties of the semiconducting silicon.

The chemistries of hydride terminated porous and flat, single crystal silicon surfaces are closely related and, with few exceptions, a novel reaction found to operate on one surface usually has some degree of success on the other.<sup>18</sup> Porous silicon is especially attractive due to its high surface area which renders analysis relatively straightforward through conventional transmission Fourier transform IR (FTIR) or diffuse reflectance IR (DRIFT) spectroscopy. As a result, routine characterization of this material is practical and facile for most chemists. Flat surfaces offer, on the other hand, a much more structurally homogeneous surface that is extremely useful for controlled reactivity studies. The general mechanistic trends for flat and porous silicon interfaces are very closely related and thus are discussed here interchangeably.

### Hydrosilylation involving a radical initiator

Hydrosilylation involves insertion of an unsaturated bond into a silicon–hydride group as shown in Fig. 4. Alkyne and alkene hydrosilylation on Si–H terminated surfaces yields alkenyl and alkyl termination, respectively. The first example of hydrosilylation of non-oxidized Si–H passivated silicon was carried out by Chidsey and coworkers in 1993 on flat crystal Si(111)

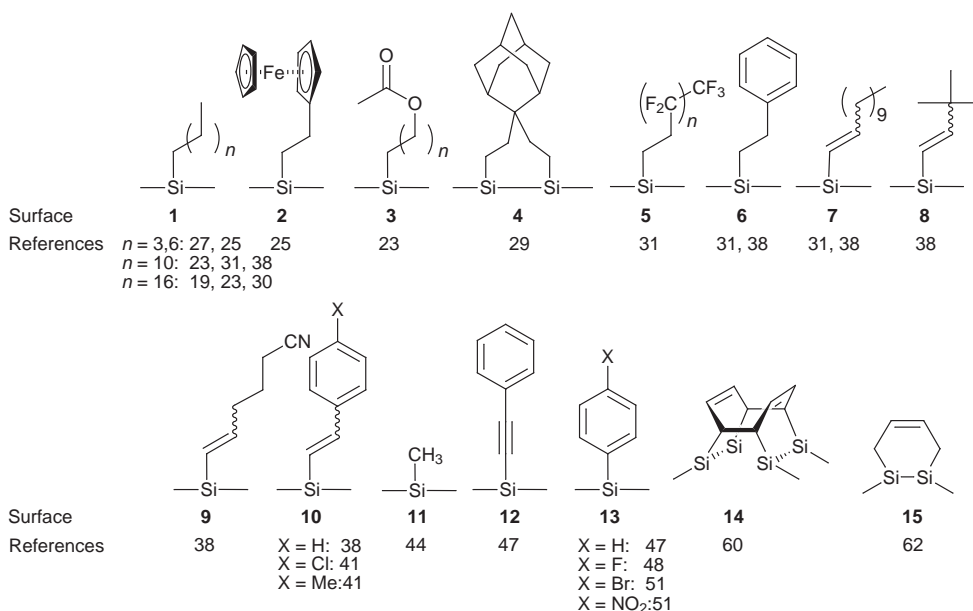
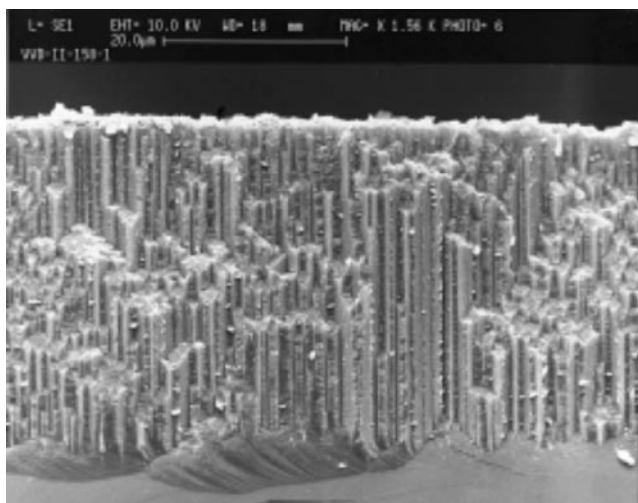
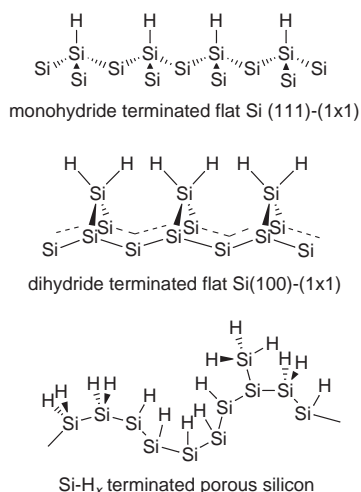


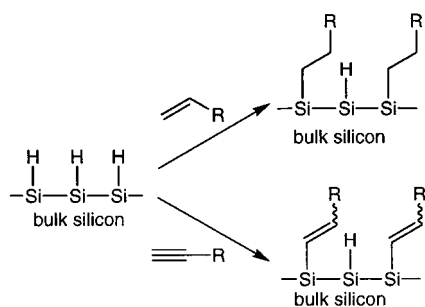
Fig. 1 Examples of organic monolayers formed on various silicon surfaces, bound through Si–C bonds.



**Fig. 2** Cross-sectional scanning electron micrograph (SEM) of a 30  $\mu\text{m}$  thick porous silicon layer electrochemically etched on a (100) single-crystal wafer. The pores here are on the order of  $\mu\text{m}$  but through variation of the etching conditions, a wide range of pore sizes (from 2 nm to  $\mu\text{m}$ ) is easily accessed. Professor M. J. Sailor is thanked for his kind permission to use this figure from ref. 2. Reproduced with permission from Wiley-VCH.



**Fig. 3** The Si(111), (100) and porous silicon hydride terminated surfaces discussed here. The flat Si(111) (1  $\times$  1) surface is capped with only one hydride to satisfy the tetravalency of the silicon atoms. The dihydride flat Si(100) (1  $\times$  1) is shown but monohydride Si(100) (2  $\times$  1) and mixed mono- and di-hydride Si(100) (3  $\times$  1) surfaces are also possible.<sup>1</sup>

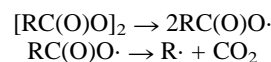


**Fig. 4** Hydrosilylation of alkenes or alkynes involves insertion of the carbon-carbon unsaturated bond into the silicon-hydride bond, yielding alkyl and alkenyl terminated surfaces, respectively.

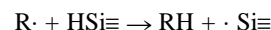
surfaces.<sup>19</sup> Insertion of alkenes into surface bound Si-H groups, in the presence of a diacyl peroxide radical initiator, provided high quality alkyl monolayers at 100  $^{\circ}\text{C}$ . Monolayers prepared from octadecene, yielding octadecyl groups on the surface (surface **1**, Fig. 1), are densely packed and tilted approximately 30 $^{\circ}$  from the surface normal. As a result of the good coverage provided by the film, the silicon surfaces demonstrate excellent

stability and withstand extended boiling in aerated chloroform, water, acid (2.5 M H<sub>2</sub>SO<sub>4</sub> in 90% dioxane, v/v) and base (10% aqueous 1 M NH<sub>4</sub>OH), and are resistant to fluoride (immersion in 48% aqueous HF). Under ambient conditions in air, little oxidation of the silicon surface is observed, indicating the usefulness of this approach for technological applications.

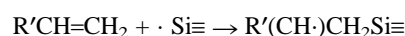
The authors propose a radical mechanism for monolayer formation under these conditions. The initiator, the diacyl peroxide, undergoes homolytic cleavage to form two acyloxy radicals which decompose to carbon dioxide and an alkyl radical.



The alkyl radical can then abstract H $\cdot$  from a surface Si-H group to produce a silicon radical.



Because silyl radicals are known to react extremely rapidly with olefins, formation of a silicon carbon bond is the next probable step.<sup>20</sup>

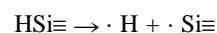


The carbon-based radical can then abstract a hydrogen atom either from a neighboring Si-H group or from the allylic position of an unreacted olefin.

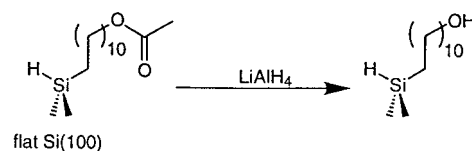
The majority of studies carried out by this group involved perhydroalkenes but the  $\omega$ -Cl terminated olefin, 11-chloroundec-1-ene, produced good quality monolayers with chloride termination. As suggested by the authors, further functionalization of the surface through the chloride is possible. Hydrosilylation of the alkyne, hexadecyne, produced a good quality monolayer and as noted in a footnote,<sup>21</sup> may be bound to the silicon surface through a vinyl group as would be expected. The use of the bromide terminated olefin, 11-bromoundec-1-ene, however, produced a poorly organized monolayer, perhaps due to the incompatibility of the Br with the radical nature of the reaction.

### Thermally induced hydrosilylation

Control experiments carried out by Chidsey and co-workers during their investigations of diacylperoxide initiated olefin hydrosilylation on Si(111) surfaces indicated that the reaction could occur in the absence of diacylperoxide initiator at higher temperatures ( $\geq 150$   $^{\circ}\text{C}$ ), almost certainly through homolytic Si-H cleavage.<sup>22</sup>



The silyl radical will then proceed to react with the olefin to form the silicon-carbon bond. This result was pursued by Sudhölter and coworkers on hydride terminated Si(100).<sup>23</sup> Working at 200  $^{\circ}\text{C}$ , a number of different olefins were examined for their propensity to form stable monolayers. 2 h contact time produced closely packed monolayers when long-chain aliphatic alkenes (12-18 C, surface **1**, Fig. 1) were used as judged by X-ray reflectivity, ATR IR spectroscopy and contact angle measurements. With  $\omega$ -ester substituted alkenes, ester terminated alkyl surfaces were prepared (surface **3**, Fig. 1) and then subsequently cleaved with LiAlH<sub>4</sub> (Scheme 1) to yield the hydrophilic, hydroxy-terminated silicon surface.



**Scheme 1**

This reaction clearly demonstrated that alkyl monolayers on silicon are robust enough to tolerate further chemical reactions,

and can be built upon directly to produce more sophisticated surfaces. Alcohol-terminated alkenes could not be utilized directly through this method because they react with the surface through the hydroxy group, yielding ill defined monolayers. Thus traditional protecting group strategies may be viable options when preparing functional films on silicon. Recent work has demonstrated that aliphatic monolayers produced on hydride terminated Si(111) and Si(100) through this reaction are also stable up to 615 K under vacuum which indicates that organic monolayers on silicon can be thermally resistant.<sup>24</sup>

Thermally induced hydrosilylation of alkynes and alkenes has been applied to Si-H terminated porous silicon surfaces. Horrocks and Houlton reported that refluxing porous silicon for 18–20 h at 110–180 °C in an aliphatic alkyne or alkene yields alkyl monolayers (surface **1**, Fig. 1).<sup>25</sup> Alkyne hydrosilylation does not produce surface bound vinyl groups as one would expect, presumably because it undergoes two hydrosilylations. Hydrosilylation of vinyl ferrocene (surface **2**, Fig. 1) was particularly interesting since it allows for electrochemical investigations of the ethylferrocene terminated surface. While these surfaces demonstrate good stability to boiling base (75% KOH–25% EtOH, pH 12), significant photoluminescence quenching due to the thermal hydrosilylation is observed (Fig. 7, *vide infra*). Porous silicon is inherently fragile and appears to degrade under extended reflux conditions.

### Photochemical hydrosilylation (UV)

It is known in the organic and organometallic literature that UV irradiation can promote hydrosilylation of unsaturated compounds<sup>26</sup> due to homolytic cleavage of Si–H bonds, as is the case with thermal induction. UV photoinduction, however, takes place at room temperature and thus provides a way to avoid thermal input which could be harmful to delicate or small features on a silicon chip. Minimal input of thermal energy would be preferable in any IC manufacturing process (thermal budget). Chidsey and coworkers showed in 1997 that irradiation of a hydride terminated Si(111) surface with UV light (185 and 253.7 nm) in the presence of an aliphatic alkene like pent-1-ene or octadec-1-ene (surface **1**, Fig. 1) brought about hydrosilylation in 2 h at room temperature.<sup>27</sup> Interestingly, these surfaces were further functionalized through a biphasic (gas/solid) photoinduced (351 nm) free radical chlorosulfonation of the terminal methyl groups and then reacted with ethylenediamine (Scheme 2).<sup>28</sup> The authors propose binding of biomolecules to the amino terminus for investigation by scanning probe microscopy (SPM), sensing, and surface related assays. UV irradiation derived from a Xe UV lamp (24 h) has also been used to hydrosilylate divinyladamantane on Si(111) surfaces for use as a solid substrate for chemical vapor deposition (CVD) of diamond films (surface **4**, Fig. 1).<sup>29</sup>

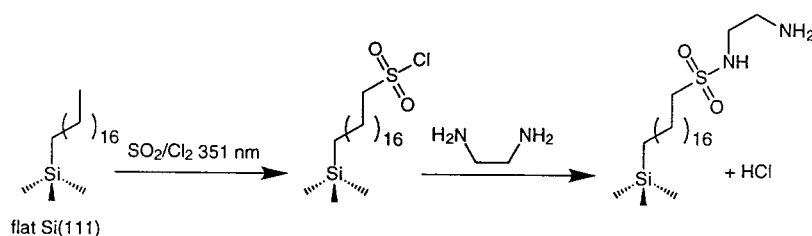
These results were followed up by Effenberger *et al.* who found that irradiation with substantially longer wavelengths, up to 385 nm, for 20–24 h were also effective in promoting alkene hydrosilylation on Si(111) surfaces (surface **1**, Fig. 1).<sup>30</sup> Using masking techniques, they photopatterned the surface to produce areas of differing wettabilities as visualized under a microscope.

### Photochemical hydrosilylation (white light)

Recently, Stewart and Buriak demonstrated that a simple white light source could induce hydrosilylation of alkenes and unconjugated alkynes on Si–H terminated photoluminescent porous silicon surfaces at room temperature in minutes.<sup>31</sup> Illumination of an unfiltered tungsten ELH bulb (GE slide projector bulb) of moderate intensity (22–44 mW cm<sup>-2</sup>) on a photoluminescent porous silicon sample wetted with an alkene or alkyne (surfaces **1**, **5–7**, Fig. 1) induces surface hydrosilylation as demonstrated schematically in Fig. 5. Because the reaction is photoinduced, photopatterning can be easily carried out with simple optical apparatus to prepare spatially defined areas of differing chemical functionalities. For instance, use of a f/75 reducing lens and a mask produced with a high quality laser printer can achieve features as small as 30 μm. Examples of larger scale photopatterning on porous silicon produced from n-type silicon crystal wafers are shown in Fig. 6. As demonstrated in Fig. 6(b)–(d) long aliphatic substituents on the surface, here dodecyl groups, can sufficiently protect the surface from boiling alkali. The remaining, unpatterned areas of Si–H termination dissolve rapidly under these conditions in what can be viewed as a lithographic process. Dodecyl terminated samples will tolerate boiling for 30 min in aerated aqueous KOH (pH 10) solution, conditions under which freshly etched (Si–H terminated) porous silicon will dissolve in seconds. These surfaces are not, however, as stable as those produced through Lewis acid mediated hydrosilylation (*vide infra*, Hydrosilylation mediated by metal complexes) which will resist several hours of contact with alkali at 100 °C. The unpatterned areas of surface Si–H groups can, instead of undergoing dissolution, hydrosilylate (white light induced) a second alkene or alkyne to produce domains of differing terminations. This provides an extremely useful method of hydrosilylating porous silicon surfaces at room temperature with simple white light illumination.

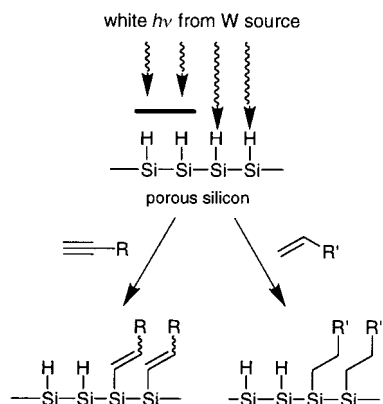
The mechanism of this reaction still remains to be determined. Monochromatic experiments indicated that the degree of incorporation increased with shorter wavelengths (450 > 550 > 650 nm) as measured by transmission FTIR. Because wavelengths as long as 400 nm will promote alkene hydrosilylation on hydride terminated Si(100) surfaces, the blue end of the white light illumination may induce homolytic Si–H cleavage to produce silicon radicals.<sup>26</sup> Alternatively, photogenerated holes on the photoluminescent porous silicon surface are produced upon light soaking which are subsequently attacked by alkyne or alkene nucleophiles.<sup>32</sup> Electron deficient alkynes (phenylacetylene, 4-methylphenylacetylene and 4-chlorophenylacetylene) require long reaction times (12 h) and are generally poorly incorporated, supporting a mechanism involving nucleophilic attack.<sup>33</sup> We are presently vigorously investigating this reaction through electron paramagnetic resonance (EPR) spectroscopy and chemical means in order to distinguish between surface radical reactions and potential involvement of the underlying electronic properties of the silicon nanocrystallites and nanowires which make up the porous silicon matrix.

The light mediated reaction appears very gentle and, depending upon the chemical groups incorporated, preserves most of the intrinsic photoluminescence of the porous silicon



Scheme 2





**Fig. 5** Illumination of photoluminescent porous silicon samples with white light in the presence of an alkene or alkyne induces hydrosilylation, yielding alkyl and alkenyl termination, respectively. The reaction takes place at room temperature in 30–60 min, with white light of moderate intensity ( $22\text{--}44 \text{ mW cm}^{-2}$ ).<sup>31</sup> Masking techniques allow for preparation of spatially defined areas of chemical functionalities.

(Fig. 7). Dodecyl groups (surface **1**, Fig. 1), having no unsaturation, maintain 97% of the photoluminescence whereas dodecenyyl termination (surface **7**, Fig. 1), bound to the surface through a vinyl group, preserves 61%. A small red shift of the photoluminescence of *ca.* 10 nm is observed. This functionalization strategy could, therefore, be important for preparation of optoelectronic porous silicon devices and sensors.

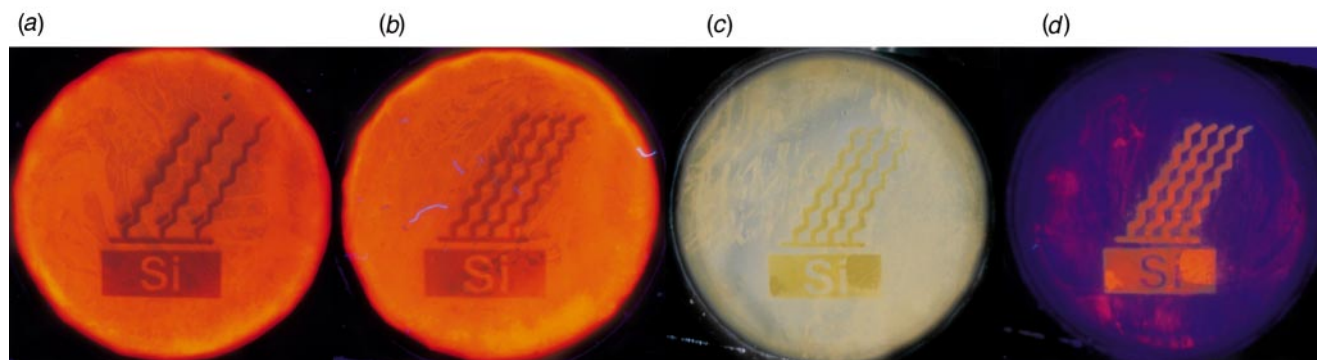
#### Hydrosilylation mediated by metal complexes

Because Pt(0) complexes and colloids are extremely effective catalysts for the hydrosilylation of alkenes with soluble, molecular silanes,<sup>34</sup> Zazzera *et al.* examined their potential on hydrogen terminated flat Si(100) surfaces.<sup>35</sup> Using 3,4-dichlorobutene as the olefin and platinum(0)-divinyltetrame-

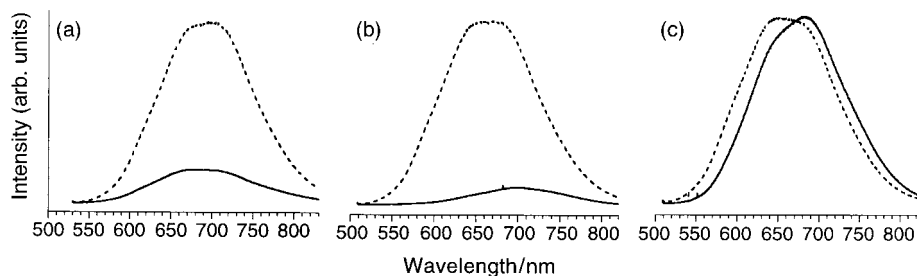
thyldisiloxane as the catalyst precursor, they observed chloride incorporation (from the Cl-containing olefin) on the surface as determined by XPS and surface mass spectrometry (TOF-SIMS) after 45 min at room temperature. *In situ* ATR IR spectroscopy indicated consumption of surface SiH<sub>2</sub> groups, supporting a hydrosilylation mechanism. They found, however, that the platinum complex also catalyzed oxidation of the silicon surface although this competing reaction could be reduced by minimizing trace water and utilizing a large excess of olefin.

Other workers have found that late transition metal complexes, in general, are problematic with respect to Si-H terminated porous silicon.<sup>36</sup> Exposure of freshly etched porous silicon to Wilkinson's catalyst, RhCl(PPh<sub>3</sub>)<sub>3</sub>, and the palladium complexes PdCl<sub>2</sub>(PEt<sub>3</sub>)<sub>2</sub> or Pd(OAc)<sub>2</sub>/1,1,3,3-tetramethylbutyl isocyanide in the presence of alkynes,<sup>37</sup> resulted in blackening of the surfaces due to apparent metal deposition which thoroughly quenched the photoluminescence. Substantial oxidation was also noted even if considerable precautions were taken.

In order to avoid late transition metals and their accompanying problems of oxidation and metal deposition on porous silicon, Buriak and Allen utilized a Lewis acid to mediate hydrosilylation of alkynes and alkenes.<sup>38</sup> Lewis acid catalyzed or mediated hydrosilylation reactions seemed ideal for functionalization of porous silicon because of the mild reaction conditions involved and high selectivity and specificity of the corresponding solution phase reaction.<sup>39</sup> AlCl<sub>3</sub> is an effective catalyst for alkenes as well which suggested that Lewis acid mediated surface chemistry would not be limited to alkynes.<sup>39b,c</sup> Since EtAlCl<sub>2</sub> is soluble in non-polar solvents whereas AlCl<sub>3</sub> is not, it was chosen as the Lewis acid to avoid multiphase reactions on the surface of porous silicon.<sup>40</sup> A wide range of alkynes and alkenes were smoothly hydrosilylated on Si-H passivated porous silicon at room temperature (surfaces **6–10**, Fig. 1), yielding vinyl and alkyl terminated surfaces, re-



**Fig. 6** Photographs of 12 mm diameter photoluminescent porous silicon samples prepared through white light promoted hydrosilylation of dodec-1-yne (surface **7**) and dodec-1-ene (surface **1**) through masking procedures.<sup>31</sup> (a) Surface **7** appears as the darkened, red-shifted patterned area when illuminated with a 365 nm hand-held UV lamp. The other areas of the wafer are unfunctionalized (native Si-H termination). (b) Surface **1** (ref-shifted patterned area) upon illumination with 365 nm light. (c) Sample from (b) after boiling in aerated, aqueous KOH (pH 12) solution for 15 s. The unfunctionalized porous silicon (grey area) has dissolved while the hydrosilylated surface (surface **1**, golden area) remains intact. (d) Illumination of the surface from (c) with a 365 nm hand held UV lamp. The PL of the hydrosilylated area (surface **1**) remains intact while most of the unfunctionalized PL is destroyed. This figure has been reproduced from ref. 31 with permission from Wiley-VCH.

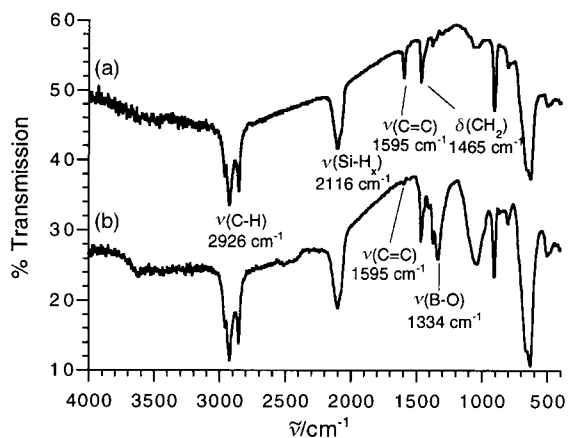


**Fig. 7** Photoluminescence spectra of 1-dodecene hydrosilylation (surface **1**) on n-type porous silicon (440 nm excitation). The dotted spectrum is that of freshly etched porous silicon, and the solid that of the resulting dodecyl terminated surface. (a) Lewis acid mediated,<sup>38</sup> (b) thermally induced (2 h reflux in neat dodec-1-ene),<sup>36</sup> (c) white light promoted (60 min reaction at  $22 \text{ mW cm}^{-2}$  white light).<sup>31</sup>

spectively. By using an excess of  $\text{EtAlCl}_2$ , alkynes with coordinating functional groups (ester, hydroxy and cyano groups) could also be incorporated onto the surface. One equivalent of the Lewis acid complexes the coordinating group and the remainder mediates the hydrosilylation reaction. We have found, thus far, the reaction to be independent of silicon doping and morphology.

The effects of the reaction on photoluminescence have been studied in some detail. In all cases, at least 75% of the intrinsic photoluminescence is lost, as shown for dodec-1-ene in Fig. 7, although it can be partially restored through boiling in alkali or soaking in HF solutions.<sup>41</sup> Conjugated functionalities, such as styrenyl termination (surface **10**, Fig. 1), result in complete loss of photoluminescence with no possibility for recovery. Neither electron donating nor withdrawing substituents (chloro or methyl) on the conjugated styrenyl group have any effect on the photoluminescence. Sailor and Song observed similar effects for phenylacetylide termination (*vide infra*, Reactions of alkyl/aryl carbanions) in which a phenyl ring is conjugated through an alkyne linker (surface **12**, Fig. 1). These results suggest that surface states associated with the conjugated group result in efficient non-radiative recombination of the excitons produced upon irradiation with blue or UV light.

That the reaction is indeed hydrosilylation is strongly supported by the following experimental results. Consumption of Si-H groups can be clearly seen through difference FTIR spectra taken before and after the reaction with an alkyne or alkene.<sup>36</sup> The procedure with dodec-1-yne produces a surface bound vinyl group whose  $\nu(\text{C}=\text{C})$  of this olefin can be clearly distinguished in the transmission FTIR at  $1595\text{ cm}^{-1}$  as shown in Fig. 8. It was proven through chemical means that this



**Fig. 8** FTIR (transmission mode) of monolayers prepared through: (a) hydrosilylation of dodec-1-yne mediated by  $\text{EtAlCl}_2$  on porous silicon resulting in covalent attachment of a dodecyl group (surface **7**) and (b) hydroboration of the surface-bound olefin of the dodecyl group with  $0.8\text{ M BH}_3\cdot\text{THF}$ . The  $\nu(\text{C}=\text{C})$  vanishes upon hydroboration, as would be expected for an olefinic substituent. Reprinted with permission from *J. Am. Chem. Soc.* (ref. 38), Copyright 1998, American Chemical Society.

functionality is indeed a double bond. The dodecyl terminated surface was hydroborated with excess  $0.8\text{ M BH}_3\cdot\text{THF}$  in THF under nitrogen followed by quenching of the surface in air and rinsing with excess THF.<sup>42</sup> Almost quantitative disappearance of the stretch at  $1595\text{ cm}^{-1}$  was observed by transmission FTIR in Fig. 8(b), with concomitant appearance of a new stretch at  $1334\text{ cm}^{-1}$  which corresponds to the B-O stretching frequency.<sup>43</sup> The stereochemistry of the borane addition has not been determined although it is expected that the boron atom will add preferentially to the least hindered carbon, that being the carbon  $\beta$  to the surface silyl group.

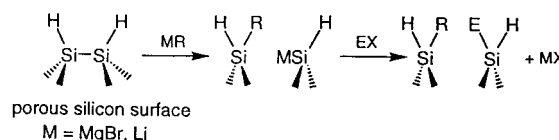
The hydrophobic, alkyl and alkenyl terminated surfaces are very stable under highly demanding chemical conditions. The dodecyl functionalized surface (surface **7**, Fig. 1) will resist at least 4 h of boiling in aerated solutions of 25%  $\text{EtOH}$ -75% aqueous  $\text{KOH}$  (pH 10) with little change in the FTIR spectrum;

Si-H terminated porous silicon dissolves in seconds. The surprising increase in photoluminescence of dodecyl and dodecyl terminated porous silicon under these conditions may be due to a secondary basic etch at defect sites although this observation remains to be clarified.<sup>41</sup> Long term stability studies under ambient conditions are underway but preliminary results indicate that dodecyl terminated porous silicon derived from p-type wafers is at least an order of magnitude more resistant to oxidation, as judged by FTIR spectroscopy. This route appears to be a promising, low temperature means of stabilizing porous silicon, and incorporating a broad range of chemical functionalities for preparation of 'smart', sophisticated silicon devices.

### Reactions of alkyl/aryl carbanions

The use of alkyl Grignard and alkyl lithium nucleophiles on silicon surfaces was first investigated by Chazalviel, Ozanam and coworkers.<sup>44</sup> Silicon-methyl terminated porous silicon derived from p-type single crystal silicon (surface **11**, Fig. 1) was demonstrated to be electrochemically accessible through treatment of the native Si-H passivated surface with a methyl Grignard or methyl lithium organometallic under anodic conditions. As proposed by the authors, silicon hydride groups are consumed through a transmetalation reaction, forming silicon-methyl groups and either  $\text{MgHX}$  or  $\text{LiH}$  as by-products of the reaction. The stability of the surfaces increases an order of magnitude with respect to accelerated air oxidation at  $100\text{ }^\circ\text{C}$  as determined by FTIR spectroscopy. This electrochemical reaction is especially interesting since it has no obvious chemical equivalent for soluble, molecular silanes;<sup>45</sup> the semiconducting properties of the underlying silicon are harnessed to effect the chemistry.<sup>46</sup>

Song and Sailor<sup>47</sup> and Kim and Laibinis<sup>48</sup> subsequently investigated the effects of Grignard and alkyl and aryl lithium reagents without an electronic bias. The range of carbanion nucleophiles that could be bound to the surface of porous silicon through Si-C bonds was extended and detailed mechanistic studies were carried out. The mechanism proposed for silicon-carbon bond formation, shown in Scheme 3, involves attack of the weak Si-Si bond ( $\text{Si-Si} = 215\text{--}250\text{ kJ mol}^{-1}$ ,  $\text{Si-H} = 323\text{ kJ mol}^{-1}$ )<sup>49</sup> by the carbanion nucleophile (MR). Soluble molecular disilanes react in a similar manner.



**Scheme 3**

The resulting silyl anion on the porous silicon surface can be further reacted with an electrophile (EX), offering the possibility to form mixed surfaces.

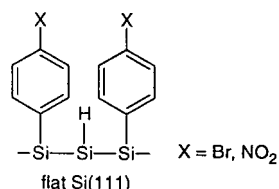
The effects of carbanion functionalization on the photoluminescence of porous silicon have also been investigated in some detail. Methyl termination, as examined by Chazalviel and coworkers,<sup>44</sup> has little effect on the photoluminescence intensity of p-type porous silicon. Sailor and Song observed that a conjugated alkyne (surface **12**, Fig. 1) results in irreversible quenching of the intrinsic photoluminescence that could not be recovered by rinsing with HF solutions. It was found, however, that simple phenyl<sup>47</sup> or 4-fluorophenyl<sup>48</sup> termination (surface **13**, Fig. 1) resulted in only minor quenching which points to the interesting possibility of using the surface functionalities to tune the photoluminescence and underlying optoelectronics of the material.

Alkylation of flat silicon surfaces with alkyl Grignards or lithium reagents through a two-step route has also been demonstrated by Lewis and Weinberg.<sup>50</sup> Chlorination of a hydride terminated flat Si(111) crystal with  $\text{PCl}_5$  for 20-60 min

at 80–100 °C produced a chloride terminated silicon surface. Transmetalation with an organolithium or Grignard at 80 °C for 30 min to 8 days produced LiCl or MgXCl, and an alkyl group bound to the silicon surface through an Si–C linkage. Surfaces with long alkyl termination are more resistant to oxidation under ambient conditions and to boiling in aerated chloroform and water. Thermal desorption and XPS experiments indicate that  $\equiv\text{Si-OR}$  linkages are not formed which provides support for the expected Si–C bond formation event.

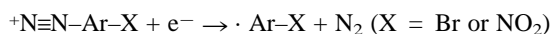
### Electrochemical diazonium reduction

Electrochemistry has also been used to produce close-packed phenyl monolayers (surface **13**, Fig. 1) on hydride terminated flat n-type Si(111) surfaces (Scheme 4).<sup>51</sup>

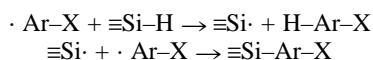


Scheme 4

Application of a negative potential of *ca.* 1 V to a dilute HF solution containing a 4-nitro- or bromo-benzene diazonium salt results in production of aryl radical and dinitrogen.



The aryl radical can then abstract a surface hydride to form silicon radicals which can react with another aryl radical to form the silicon–carbon bond.



The covalent nature of the phenyl bonding to the surface is demonstrated by their stability to aqueous 40% HF solutions, and XPS and Rutherford backscattering (RBS) measurements. Because this reaction utilizes the electrode nature of the semiconducting silicon, no clear reaction parallels can be found for soluble, molecular silanes. One important advantage of this approach is that the process is cathodic, thus making the surface electron rich during the reaction which renders it less susceptible to nucleophilic attack by water, suppressing oxidation.

### Ultra high vacuum (UHV) functionalization strategies

The reactivity of clean silicon surfaces, in absence of a hydrogen monolayer, has been studied intensively by a number of groups under ultra high vacuum (UHV) conditions.<sup>1</sup> The activity of these surfaces is very different from that of the metastable Si–H terminated materials which provides further insight into the structures and properties of flat silicon. The thermally reconstructed Si(100) (2 × 1) surface (Fig. 9), with no

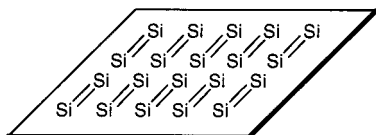


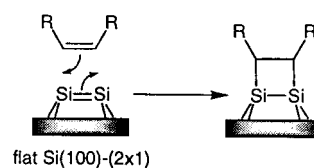
Fig. 9 Schematic diagram of the Si=Si dimers oriented on a Si(100) surface under UHV conditions.

hydrogen capping, has recently been shown to be capable of a number of remarkable cycloaddition reactions that have parallels to organic reactions. The surface silicon atoms pair into dimers connected by a  $\sigma$  and a  $\pi$  bond, thus having essentially double bond character. Use of 4° miscut off-axis Si(100) single crystal wafers allows for highly rotationally

oriented samples in which all the Si=Si dimers are pointed in the same direction, yielding anisotropic surfaces on a centimeter length scale. The silicon–silicon double bonds are highly reactive, and have been exploited to produce ordered monolayers through the chemistry described here.

### [2 + 2] Reactions of alkynes and alkenes with reconstructed Si(100)

Early work on ‘relatively simple’ unsaturated hydrocarbons such as ethylene, propylene, acetylene and benzene have been shown to chemisorb on Si(100) (2 × 1) surfaces and are able to resist temperatures of up to 550–600 K.<sup>52</sup> It was suggested that alkenes add to clean Si(100) (2 × 1) surfaces to form a disilicon substituted aliphatic  $-\text{CH}_2\text{CH}_2-$  bridge through a formal [2 + 2] cycloaddition (Scheme 5).



Scheme 5

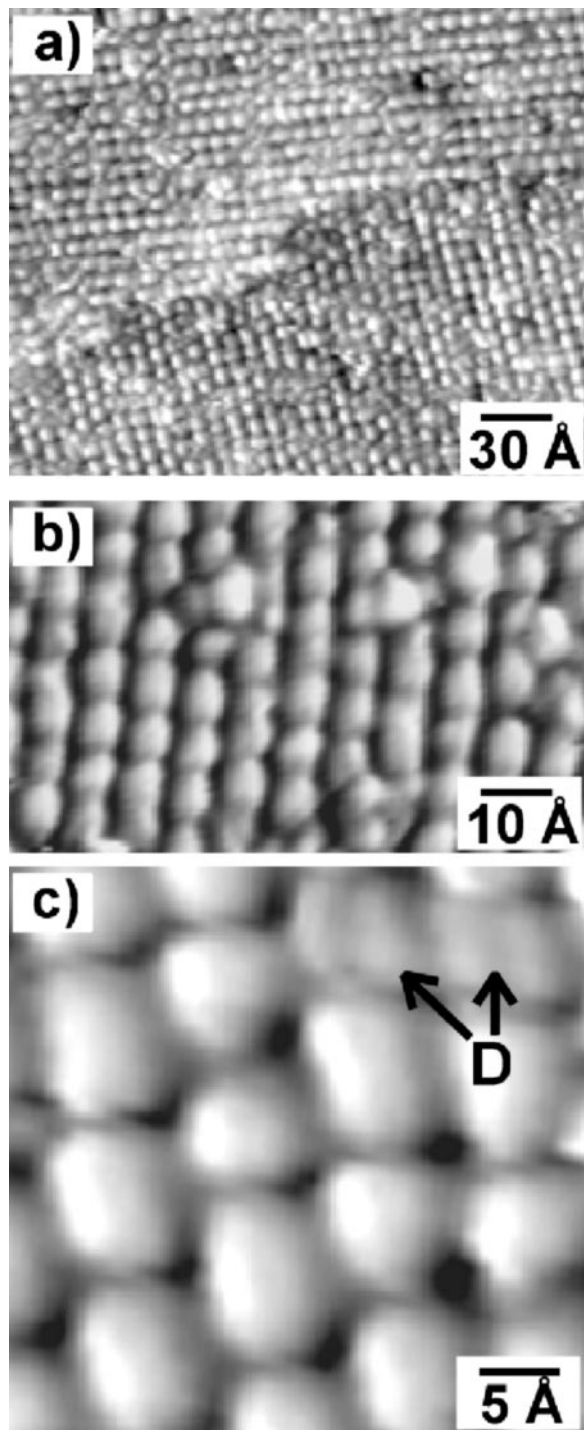
Two new Si–C  $\sigma$  bonds form due to cleavage of the  $\pi$  bonds in the alkene and disilylene. Electron energy loss spectroscopy (EELS) suggests rehybridization of the two  $\text{sp}^2$  carbons to  $\text{sp}^3$  although the fate of the remaining Si–Si  $\sigma$  bond is still unclear.<sup>53</sup> Acetylene reacts in a similar [2 + 2] fashion yielding a disilicon-substituted alkene and involves a change in hybridization at the carbon from  $\text{sp}$  to  $\text{sp}^2$  in this case.<sup>54</sup> Concerted [2 + 2] cycloadditions are symmetry-forbidden which suggests a low-symmetry pathway.<sup>55</sup>

Hamers *et al.* have recently described an elegant extension of this series of reactions involving the  $\pi$  bonds of organic species containing C=C bonds.<sup>56</sup> A wide range of complex cyclic olefins react in this manner at moderate temperatures (50–100 °C), including cyclopentene,<sup>57</sup> 3-pyrroline,<sup>53</sup> pyrrolidone,<sup>58</sup> norbornadiene,<sup>53</sup> cycloocta-1,5-diene,<sup>59</sup> and cyclooctatetraene.<sup>60</sup> The [2 + 2] addition of cyclooctatetraene (surface **15**, Fig. 1) is especially interesting since it appears to add to the surface through a double cycloaddition, leaving two alkene groups per molecule exposed through which further chemistry could be carried out.<sup>60</sup> Scanning tunneling microscopy (STM) images of the cyclooctatetraene functionalized surface are shown in Fig. 10, revealing the long range order of the samples and formation of only one major surface species.

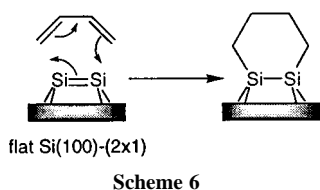
### Diels–Alder ([4 + 2]) reactions of dienes with reconstructed Si(100)

Konecny and Doren predicted,<sup>61</sup> and Bent and coworkers demonstrated experimentally,<sup>62,63</sup> that the double bond character of the reconstructed Si(100) (2 × 1) surface could act as a dienophile in a Diels–Alder [4 + 2] type reaction (Scheme 6).

Chemisorption of buta-1,3-diene (surface **15**, Fig. 1) or 2,3-dimethylbuta-1,3-diene onto the Si(100) (2 × 1) surface at room temperature results in an efficient Diels–Alder reaction, forming two Si–C  $\sigma$  bonds and one unconjugated, internal olefin. FTIR spectroscopy, thermal desorption, near edge X-ray absorption fine structure and deuterium labeling studies assisted in the determination of surface composition. A reinvestigation of the 2,3-dimethylbuta-1,3-diene reaction on Si(100) (2 × 1) by Hamers and coworkers supports the observation of a Diels–Alder [4 + 2] cycloaddition for 80% of the molecules although they note a minor (20%) [2 + 2] cycloaddition product as well.<sup>64</sup>



**Fig. 10** Scanning tunneling microscopy (STM) images of the Si=Si dimer terminated Si(100) surface after exposure to cyclooctatetraene to form surface **15** (Fig. 1); (a) demonstrates the long range anisotropy and ordering of the surface while (b) and (c) reveal the absorption pattern of the molecules. 'D' refers to a minority species comprising < 5% of the surface features. Professor Robert J. Hamers is gratefully acknowledged for permission to reproduce this figure from ref. 60(a). Reprinted with permission from *J. Phys. Chem.* (ref. 60(a)), Copyright 1998, American Chemical Society.



In the case of cyclohexa-1,3-diene, 55% of the surface products arise from the [4 + 2] addition, 35% the [2 + 2] and 10% and

unknown product. The [4 + 2] products are predicted to be thermodynamically more stable but because surface temperature has little effect on product distributions, it is suggested that the reaction is under kinetic control.

### Directions for functionalized silicon surfaces: present and future

Tunable, stabilized silicon surfaces will have a broad array of technologically important applications. Flat, non-oxidized silicon surfaces functionalized with ordered organic monolayers have obvious potential in microelectronics. Gate oxides in metal oxide semiconductor transistors (MOSFETs) may be replaced with an organic monolayer since the resistivity could be modulated through organometallic/organic synthesis.<sup>56</sup> Aliphatic substituents will provide obvious insulating properties but conjugated, unsaturated organic moieties could allow for fine tuning of the surface conductivity. Interfacing of silicon microelectronic circuits with neuronal networks and other biologically relevant systems is a fascinating direction that has received much attention in recent years.<sup>65</sup> Surface properties are crucial and thus the power of organometallic/organic chemistry on silicon could play an important role.

Functionalized, stable porous silicon surfaces have an immense variety of potential uses which partially explains the explosion of interest in this material since 1990.<sup>2,5</sup> Applications include use as chemical sensors,<sup>66</sup> microelectronics,<sup>67</sup> photonics,<sup>68</sup> optoelectronic devices<sup>13</sup> such as electroluminescent displays,<sup>69</sup> photodetectors,<sup>13</sup> and as a matrix for photopumped tunable lasers.<sup>70</sup> The biocompatibility of porous silicon has been examined *in vivo* and *in vitro* within a simulated body fluid (SBF) environment.<sup>71</sup> Hydroxyapatite, a major constituent of bone, forms on the porous silicon surface and thus is a bioactive material with interesting applications as a biological implant.<sup>72</sup>

Porous silicon as a sensor is a particularly exciting application because of its high surface area which can render it more sensitive than a flat silicon chip, and the two (at least), unrelated signal transduction modes (read-out mechanisms) that are accessible. Early observations by Sailor and coworkers indicated that physisorbed molecular adsorbates such as methanol, benzene, dichloromethane (from the vapor or as a liquid)<sup>73</sup> or NO<sup>74</sup> on the native Si-H terminated porous silicon surface reversibly quench the photoluminescence. Thus quenching of the photoluminescence could serve as a visible wavelength read-out for sensing of chemical vapors or gaseous molecules in general. The second signal transduction mode for a porous silicon-based sensor involves an optical interferometric event, unrelated to the previously described photoluminescence quenching scheme.<sup>75</sup> Thin porous silicon films exhibit Fabry-Perot fringe patterns created by multiple reflections of white light on the air-porous silicon and porous silicon-bulk silicon interfaces. A change of the index of refraction of the porous silicon matrix, induced by absorbance of a material with a different index of refraction within the pores, will cause a shift in the fringe pattern. Oxidized porous silicon has been functionalized with a number of biologically relevant molecules such as biotin and has been shown to sense and quantify streptavidin binding.<sup>75</sup> Clearly, for exquisitely selective and sensitive binding, surface chemistry is of extreme importance since binding groups must be incorporated. The organometallic chemistry described here on non-oxidized silicon surfaces is highly relevant to the preparation of sensors because of the high sophistication of these surfaces and excellent stability required.

Recent work by Whitesides and coworkers has outlined a fascinating approach towards generation of small structures through soft lithography.<sup>76</sup> An elastomer stamp or mold is used to repeatedly and accurately pattern self-assembled monolayers



(SAMs) on surfaces, producing spatially defined arrays of chemical functionalities and interface characteristics. Recent work has demonstrated the compatibility of soft lithographic techniques with standard SiO<sub>2</sub>/Si fabrication processes.<sup>77</sup> At this writing, however, no results concerning utilization of soft lithography to form monolayers on non-oxidized silicon have been revealed in the literature, but with the strong technological interest in preparing small features of tunable electronic and chemical characteristics on oxide-free silicon, it is almost certainly only a matter of time.<sup>78</sup> Several room-temperature processes involving monolayer preparation through Si-C bonds, as described here, are under development and could be applicable to soft lithography.

## Conclusions

The development of novel, organometallic reactions on non-oxidized silicon is clearly an exciting, rapidly growing field still in exploratory stages. A number of unrelated approaches have been pursued through wet chemical, electrochemical, and UHV techniques, generating preliminary trends and contributing to a better understanding of the technologically important silicon surface. The goal of exercising perfect control over the surface characteristics of silicon is a tempting one which promises both academic and commercial rewards.

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- 78 In Table 4 of ref. 76, Xia and Whitesides summarize the solid substrates and molecular precursors that form self-assembled monolayers (SAMs). The work of the groups of Chidsey (ref. 19) and Lewis (ref. 50) is mentioned.

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