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Dehydrogenative Silane Coupling on Silicon Surfaces via Early Transition Metal Catalysis

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Derivatization of silicon surfaces is an area of intense interest due to the centrality of silicon in the microelectronics industry and because of potential promise for a myriad of other applications. In this paper, we investigate the feasibility of Si–Si bond formation directly on the surface to contrast with the more widely studied Si–C and Si–O bond forming reactions. Functionalization of hydride-terminated silicon surfaces with silanes is carried out via early transition metal mediated dehydrogenative silane coupling reactions. Zirconocene and titanocene catalyst systems were evaluated for heterocoupling of a molecular silane, $RSiH_3$, with a surface Si–H group on Si(s). The zirconocene catalysts proved to be much more reactive than the titanium system, and so the former was examined exclusively. The silanes, aromatic or aliphatic, are bonded to the silicon surface through direct Si–Si bonds, although the level of incorporation of the trihydroarylsilanes was substantially higher than that of the aliphatic silanes. The reaction proceeds on nanocrystalline hydride-terminated porous silicon surfaces, as well as flat Si(100)–H_x and Si(111)–H interfaces. The reactions were studied by a variety of techniques, including FTIR, SIMS, and XPS.

Introduction

Derivatization of silicon and other semiconductor surfaces is an area of intense research because of the potential of hybrid organo-silicon structures as the basis for integrating functional materials,[1] such as polymers,[2] inorganic nanoparticles,[3] and biomolecules such as DNA, carbohydrates, and proteins, directly with silicon.[4] Another driving force for understanding silicon surface chemistry is more fundamental—do a surface and a molecule, each containing similar functional groups, react in the same manner, via the same mechanism?[1a] Reactivity in molecular and surface systems is not necessarily analogous, even if they involve the same functional groups. For instance, alkene and alkyne hydrosilylation on hydrogen-terminated silicon surfaces, when assisted with white light,[5] is mediated by excited-state species obtainable only in a crystalline silicon lattice, and thus, this reaction has no obvious parallels with the known chemistry of silane molecules, R_3SiH.[6] Differences between silicon surfaces and silane molecules include steric and electronic

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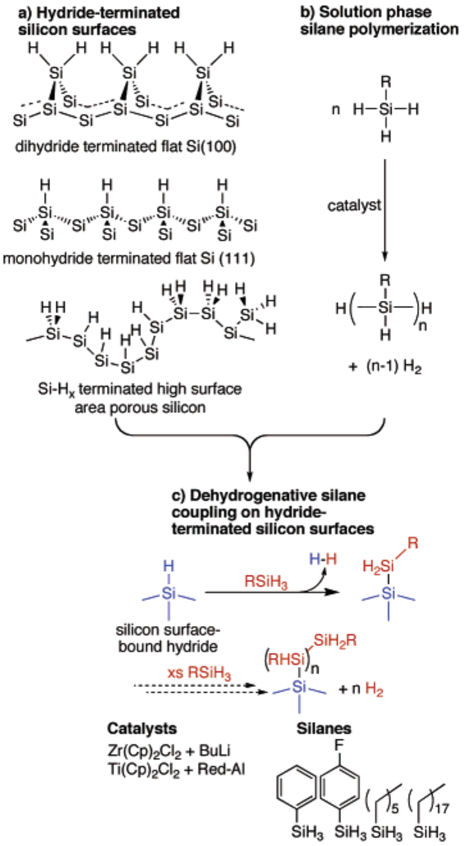
Scheme 1. (a) Representations of the Hydride-Terminated Silicon Surfaces Studied. (b) Schematic of the Solution-Phase Dehydrogenative Silane Polymerization Reaction. (c) Coupling the Hydride-Terminated Silicon Surfaces via a Dehydrogenative Heterosilane Coupling, Resulting in a New Surface Si−Si Bond.[a]



[a] The possibility of subsequent polymerization, although unlikely due to steric hindrance, needs to be considered.

effects, influence of the band structure of the underlying silicon, and others.

Here we describe an early transition metal catalyzed dehydrogenative coupling reaction of primary silanes with hydrogen-terminated silicon surfaces (Scheme 1). In solution, this chemistry leads to formation of linear silane polymers with a −Si−Si− backbone via a disproportionation reaction of Si−H bonds to Si−Si and H−H bonds.[7−9] Hydrogen-terminated silicon surfaces are well known and easy to prepare through exposure to a fluoride source, and thus, the surface Si−H group could potentially react like the Si−H group in a silane molecule.[1a] In the presence of catalyst and silane, a heterocoupling reaction would form a new surface-bound Si−Si bond between the molecular silane and the silicon surface. Even if the heterocoupling reaction is unfavorable compared to solution-phase homocoupling, a large excess of molecular silane and catalyst would be expected to drive the surface heterocoupling to maximum coverage. An earlier approach toward Si−Si bond formation on silicon surfaces was studied under ultrahigh vacuum conditions (UHV) (10^{-10} Torr) on a ‘naked’ Si(100) 2 × 1 reconstructed surface.[10] SiR_2H_2 on this interface adds across a silicon−silicon surface dimer, leading to an $-SiR_2H$ group and a surface-bound hydride. These conditions are entirely different from the wet chemistry described here on the air-stable (for minutes, at least) hydride-terminated silicon surface.

From a materials chemistry perspective, coupling of silanes directly to silicon surfaces and the nanocrystalline silicon in porous silicon and silicon nanoparticles is particularly interesting. Polysilanes, for instance, have been known for decades to be conducting and to have photoluminescent properties that are being tapped for molecular electronics and sensing applications.[11] The grafting of polysilanes to silicon via long-chain alkoxy monolayers in order to isolate the molecules for further study of their optical and conformational properties is known.[12] In this paper, however, we endeavor to produce direct Si−Si bonds; in addition to our motivation to further chart the reactivity of silicon surfaces, from a practical perspective we wish to produce a $Si_{surface}-Si_{molecule}$ bond that would be expected to be of low polarity and, thus, may provide an interesting and useful mode to link molecules directly to the silicon lattice.

Experimental Section

Generalities. All air-sensitive procedures were carried out in a nitrogen-filled Vacuum Atmospheres glovebox or with standard Schlenk techniques under argon. Dry, oxygen-free solvents were employed throughout for all organic/organosilicon syntheses and silicon-surface functionalization. Water was obtained from a Millipore system (resistivity > 18 MΩ). Si(100) (n-type, P-doped,

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$\rho = 0.5-1\ \Omega\cdot$cm) or Si(111) (n-type, P-doped, $\rho = 10-30\ \Omega\cdot$cm) wafers were purchased from SQI. Solvents were Optima grade (Fisher) and were further purified, dried, and degassed on a Pure/Solv solvent purification system. Hydrosilylation of alkynes on porous silicon were carried out exactly as published previously.

Characterization. FTIR spectra of porous silicon and polysilanes were collected using a Nicolet Nexus 760 spectrometer with a DTGS detector and a nitrogen-purged sample chamber, with 32 scans at 4 cm^{-1} resolution. Absorption spectra of flat silicon were obtained using a Nicolet Nexus 760 FTIR spectrometer with a Harrick Scientific Corporation grazing-angle attenuated total reflection (GATR) attachment (65° incidence angle). The atomic force microscope used in this study was a Nanoscope IV (Digital Instruments/Veeco) using commercially available Si cantilevers. Images were acquired in contact mode. XPS (Kratos Axis 165) was performed using the monochromatic Al Kα line with a photon energy of 1486.6 eV. The instrument was calibrated with C 1s. TOF-SIMS analysis was carried out with an ION-TOF (GmbH) 100 instrument. The dual-beam profiling mode was used—sputtering with a rastered Cs$^+$ source at 1 keV led to a crater size of 150 μm × 150 μm, with analysis by Ga$^+$ at 25 keV, 35 μm × 35 μm. Solution-phase NMR spectra were obtained on a Varian Innova 300 MHz two-channel spectrometer.

Porous Silicon Etching. Standard procedures from the literature were utilized.[13,14] A 0.28 or 1.1 cm^2 exposed area of a polished, crystalline n-type silicon wafer was etched for 3 min in a Teflon cell at 75 mA/cm^2 (positive bias) under 30 mW/cm^2 white light illumination derived from a 300 W tungsten filament ELH bulb, using 1:1 49% HF(aq)/EtOH as the electrolyte/etchant. After being etched, the porous silicon samples were rinsed copiously with ethanol followed by pentane and dried under a gentle nitrogen flow.

Flat Single-Crystal Silicon Preparation. Si(111) and Si(100) wafers were cut to size (~1 cm^2) and then cleaned via the standard RCA procedure reference:[15] Silicon shards were degreased with commercially available dish soap and then placed into a preliminary cleaning solution of 3:1 parts by volume of hot concentrated H_2SO_4/H_2O_2 (aq, 30%) for 30 min. In the first treatment, the wafers were placed in a solution of 7:2:1 parts by volume of hot H_2O/H_2O_2 (aq, 30%)/NH_4OH (aq, 27%) for 20 min. For the second stage of the treatment, the wafers were immersed in a solution of 2:1:8 parts by volume of hot H_2O_2 (aq, 30%)/HCl (aq, 37%)/H_2O for 20 min. After the cleaning process, the wafers were then placed in a 5% HF (aq) solution for 3 min to create the hydride-terminated surface or a degassed 40% NH_4F(aq) solution from Transene for 4−6 min.[16] The hydride-terminated surfaces were immediately dipped into water for several seconds. Teflon beakers and forceps were exclusively used in the steps listed above.

Reagents. Cp_2MCl_2 (M = Ti and Zr), Red-Al, and *n*-BuLi were purchased from Aldrich Chemical Co. and used as received. Phenylsilane and hexylsilane (Aldrich) were extensively sparged with Ar and then taken into the glovebox and passed over neutral dry alumina. Trichloro(4-fluorophenyl)silane was prepared according to a literature preparation.[17] The conversion of trichloro groups to trihydro groups to produce *n*-octadecylsilane and 4-fluorophenylsilane was adapted from a literature preparation of *n*-dodecylsilane from the corresponding *n*-dodecyltrichlorosilane.[18]

As an example, the procedure for synthesis of *n*-octadecyltrihydrosilane is as follows. *n*-Octadecyltrichlorosilane from United Chemical Technologies, $(C_{18}H_{37})SiCl_3$ (4 g, 0.013 mmol), was added dropwise, with stirring, to $LiAlH_4$ (1 g, 0.026 mmol) in 120 mL of diethyl ether in a 500 mL round-bottom flask cooled in an ice bath. After the addition was complete, the resulting mixture was allowed to warm to room temperature and was heated to reflux overnight. The resulting white precipitate was then allowed to settle, and the supernatant ether solution was decanted via cannula to a beaker containing HCl(aq) (3 M, 90 mL), cooled in an ice bath. The mixture was allowed to stir for 45 min, and then the organic layer was extracted. The aqueous layer was washed with diethyl ether (3 × 100 mL), and the combined organic fractions were dried over $MgSO_4$ and filtered. Most of the ether was removed by rotary evaporation, and the resulting concentrate was distilled under vacuum (85 °C, 0.005 mmHg) to yield a clear, colorless liquid.

Polysilane Syntheses. The polysilanes were prepared according to literature procedures[7e,19] and were carried out for the most part in the dark: A 2.5 M solution of BuLi in hexane (0.1 mL, 0.25 mmol) was added to the solution of zirconocene dichloride, Cp_2ZrCl_2 (0.125 mmol), in 1 mL of toluene at 0 °C. The mixture was stirred at room temperature for 30 min, accompanied by a gradual color change from light yellow to dark brown. After removal of the solvent in a vacuum, the silane $RSiH_3$ (R = Ph, 4-florophenyl, *n*-C_6H_{13}, and *n*-$C_{18}H_{37}$) was then added. The solution turned light yellow from brown with evolution of hydrogen. After 1 day, the sample was dissolved in toluene and passed through a short plug of dry florisil to remove catalyst. Toluene was removed under vacuum to yield off-white to transparent, extremely viscous oils.

Grafting of Silanes on Silicon Surfaces with the Zirconocene-Based Catalyst. Zirconocene dichloride (0.0018 g, 0.0062 mmol) was suspended in 40 μL of toluene at 0 °C to which was added a 2.5 M solution of BuLi in hexanes (5 μL, 0.0124 mmol). The mixture was stirred at room temperature for 5 min; the color gradually changed from light yellow to dark brown. At this point, the optimal procedure varies with respect to the silane, as described below. The molar ratio for the reaction also depends on the silane, as follows. Phenylsilane or 4-fluorophenylsilane/catalyst ratio is 20:1; *n*-hexylsilane:catalyst ratio is 10:1; *n*-octadecylsilane:catalyst ratio is ~4−5:1.

Procedure for aliphatic silanes, *n*-octadecylsilane, and *n*-hexylsilane on porous Si: The *n*-octadecylsilane (10 μL, 0.028 mmol) or *n*-hexylsilane (10 μL, 0.062 mmol) was added directly to the brown catalyst solution in a vial and allowed to sit for 20 min. This mixture was then dropped upon the porous silicon sample, held in a sealed homemade Teflon cell for 4 h. The sample with *n*-octadecylsilane was then rinsed with ethanol, toluene, 0.1 M HCl in diethyl ether, THF, and CH_2Cl_2, sequentially.

Procedure for aromatic silanes, phenylsilane, and 4-fluorophenylsilane on porous Si: The catalyst solution was dropped directly onto the porous silicon surface followed by half the required amount of phenylsilane or 4-fluorophenylsilane. After 30 min, the second equivalent of phenylsilane or 4-fluorophenylsilane was added to the porous silicon surface and left for 4 h to react. The samples were then rinsed with THF and CH_2Cl_2.

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Procedure for grafting silanes on flat H-terminated Si(100) and Si(111): For phenylsilane and 4-fluorophenylsilane, the catalyst solution was dropped onto the flat silicon surface followed by half the required amount of phenylsilane or 4-fluorophenylsilane (8 μL, 0.065 mmol). After 30 min, the second portion of phenylsilane or 4-fluorophenylsilane (8 μL, 0.065 mmol) was dropped onto the flat silicon surface and the reaction left for 24 h. The samples were then brushed lightly with cotton-tipped swabs soaked in toluene and ethanol, sequentially.

Grafting of Silanes on Silicon Surfaces with the Titanocene-Based Catalyst.[19] Cp_2TiCl_2 (0.0022 g, 0.0055 mmol) and Red-Al (1.5 μL, 0.0058 mmol) in 40 μL toluene were added on the porous silicon surface followed by the addition of *n*-octadecylsilane (20 μL, 0.056 mmol) and left to sit for 4 h. The sample was rinsed with THF and CH_2Cl_2.

Results and Discussion

The first surface investigated was hydride-terminated porous silicon, followed by flat Si(100)$-H_x$ and Si(111)$-$H. Porous silicon is an ideal material with which to begin analysis of new silicon surface chemistry because of the very high signal-to-noise ratio for FTIR and TOF-SIMS, thanks to its high surface area.[1a,20,21] The surface, as shown by transmission-mode FTIR (Figure 1a) is capped entirely by Si$-H_x$ groups; the tripartite structure of the $\nu(SiH_x)$ mode at ~2100 cm^{-1} results from the fact that the surface hydrides exist as $\equiv$Si$-$H, $=SiH_2$, and $-SiH_3$ groups within the porous structure (Scheme 1a).

Two different sets of catalysts were examined for surface Si$-$Si bond formation, both early transition metal based. Zirconocene and titanocene complexes are well established to catalyze Si$-$Si bond formation in molecular silanes through dehydrogenative polymerization;[7−9,19] while very effective, late transition metal complexes[18] unfortunately had to be avoided due to their propensity to be reduced to zerovalent metal upon contact with porous silicon.[22] Both the Zr and Ti catalyst systems are very rapid for molecular silane coupling at room temperature, with vigorous hydrogen evolution. The active species for these complexes is either a 14 e^- Cp_2MR^+ cation (M^{IV}) that most likely proceeds via a σ-bond metathesis reaction,[8] or a M^{III} complex that may react via an oxidative addition/reductive elimination mechanism.[7] The zirconocene catalyst system was prepared in a method similar to that previously reported for dehydrogenative polymerization by Harrod,[7] Tilley,[8] and Corey.[9] Many slight variations in the experimental details were tried to maximize silane incorporation and minimize silicon surface oxidation, including adding small amounts of toluene, dropping the catalyst solution directly to the porous silicon followed by silane, adding the silane first followed by active catalyst solution, and premixing of active catalyst and silane for various lengths of time. Addition of 1 equiv of $B(C_6F_5)_3$ with respect to zirconocene to the catalytic mixture led to low incorporation levels and was not pursued further.[7e]

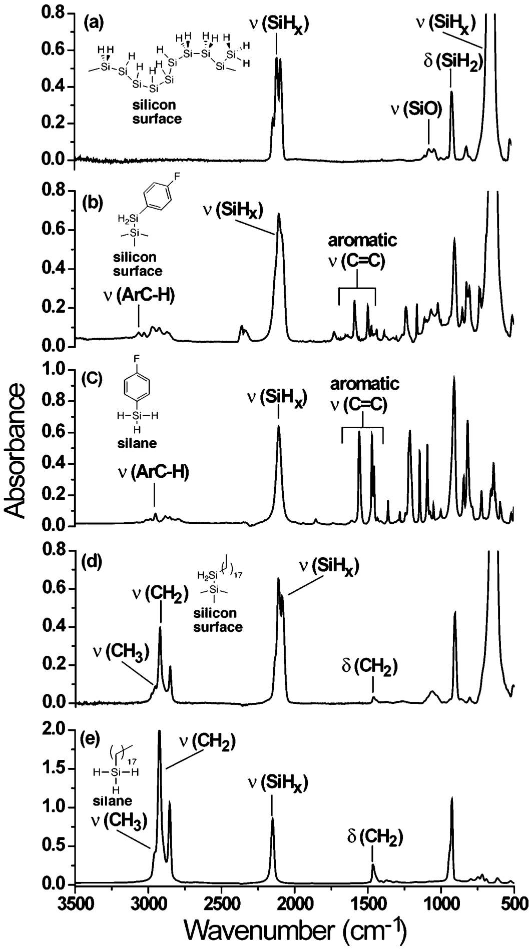

Figure 1. Transmission FTIR spectra of (a) freshly etched, Si$-H_x$-terminated porous silicon; (b) 4-fluorophenylsilane-terminated porous silicon prepared with a zirconocene-based catalyst, (c) neat 4-fluorophenylsilane sandwiched between two KBr plates, (d) *n*-octadecylsilane-terminated porous silicon prepared by zirconocene-based catalyst, and (e) neat *n*-octadecylsilane sandwiched between two KBr plates.

FTIR spectroscopy of porous silicon in transmission mode was used to determine relative levels of oxidation and silane incorporation. Oxidation was analyzed by monitoring the ν(Si$-$O) stretch at ~1100 cm^{-1} and the oxidation back-bonded ν(Si$-$H) stretches around 2200 cm^{-1}. The various IR modes associated with the organic moieties of the silanes compare favorably with monosilanes and the corresponding homopolysilane polymers (Supporting Information), prepared with the same zirconocene-based catalyst under standard literature conditions. The FTIR spectra of porous silicon surfaces functionalized with 4-fluorophenylsilane and *n*-octadecylsilane and corresponding monosilanes are shown in Figure 1. For 4-fluorophenylsilane, the two strong aromatic ring modes appear at 1592 and 1499 cm^{-1} on the porous silicon surface and at 1593 and 1499 cm^{-1} in the monosilane. For *n*-octadecylsilane, the ν(C$-$H) profile on the surface and in the monosilane are identical, with a strong $\nu(C-H)_{as}$ mode at 2923 cm^{-1}, and correspond to a linear 18-carbon aliphatic chain.

The titanocene/Red-Al catalyst unfortunately did not lead to any observable incorporation, based on the transmission FTIR spectra. Instead, intense vibrations associated with the

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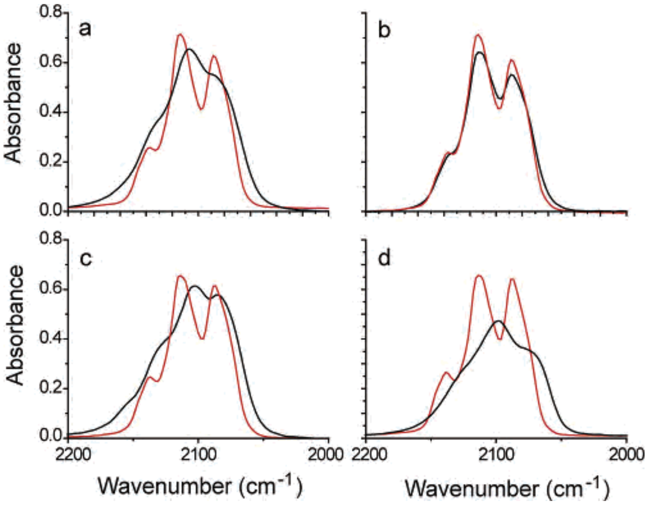


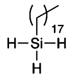
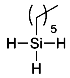
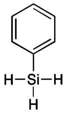
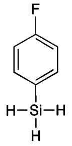
Figure 2. Transmission FTIR spectra of $\nu(\mathrm{SiH}_x)$ regions—the red spectra correspond to freshly etched porous silicon before functionalization and the black to the subsequently derivatized sample: (a) functionalization with 4-fluorophenylsilane and (zirconocene-based catalyst), (b) functionalization with *n*-octadecylsilane (zirconocene-based catalyst), (c) functionalization with phenylsilane (zirconocene-based catalyst), and (d) upon reaction with *n*-octadecyne and $EtAlCl_2$ (hydrosilylation, leading to consumption of Si−H groups).

Red-Al were observed and could not be removed with copius rinsing with organic solvents. A dilute HF(aq) rinse leads to a clean porous silicon spectrum but did not uncover any weak silane absorbances. As a result, all further efforts were focused exclusively upon the zirconocene system.

The integrated intensity of the $\nu(\mathrm{SiH}_x)$ vibration has been used for semiquantitative estimation of coverage.[13,23] For the commonly studied hydrosilylation reaction of alkenes/alkynes, Si−H groups are consumed, and thus the $\nu(\mathrm{SiH}_x)$ integrated intensity decreases in the FTIR spectrum. With this trihydrosilane coupling reaction, on the other hand, the $\nu(\mathrm{SiH}_x)$ intensity *increases* since the $RSiH_3$ attachment reaction consumes one surface Si−H but leaves two bonded to the original silane (Scheme 1c). Figure 2 shows the $\nu(\mathrm{SiH}_x)$ profile for porous silicon reactions. As can be seen in Figure 2a−c, coupling of the silanes via the zirconocene-catalyzed reaction leads to a broadening of the ν(Si−H) and an increase in the integrated area, although for *n*-octadecylsilane, the representative aliphatic silane, the change is only minor. Spectrum d of Figure 2, in contrast, shows the $\nu(\mathrm{SiH}_x)$ region after having undergone a Lewis acid ($EtAlCl_2$)-mediated hydrosilylation reaction with 1-octadecyne; in this case, the $\nu(\mathrm{SiH}_x)$ region decreases by 12% due to consumption of silicon hydrides.

Table 1 summarizes the observed average increases of the integrated $\nu(\mathrm{SiH}_x)$ region for all four silanes examined here. The $\mathrm{Si-H}_x$ stretch region is used as a relative index of reaction progress in absorbance-mode FTIR, according to the equation in Table 1. An important assumption is made for all semiquantitative analyses of $\nu(\mathrm{Si-H}_x)$ intensities, most specifically concerning the relative integration of different Si−H stretches; at the very least, this approach is useful for relative comparisons, as is done here.[13,23] The aromatic derivatives, phenylsilane and 4-flurorophenylsilane, show the highest overall increase of the $\nu(\mathrm{SiH}_x)$ intensity, of 14−19%, while the alkyl silanes, *n*-octadecylsilane, and *n*-hexylsilane, are substantially lower. The octadecylsilane ν(C−H) stretches in the 2900−3000 cm^{-1} region appear quite strong (Figure 1d) due to the 37 C−H bonds; this is, however, deceptive, and coverage on porous silicon is in fact low. Recent work by Zuilhof and Südholter has shown how the ν(C−H) can complement the $\nu(\mathrm{SiH}_x)$ to determine incorporation, and integration of the 37 C−H bonds here leads to a calculated incorporation level of about 4%.[23] The higher incorporation levels of aromatic silanes versus aliphatic silanes is to be expected, as phenylsilane is much more reactive in the molecular case as well;[8] adding to the intrinsic lowered reactivity of aliphatic silanes, the high steric hindrance of the surface, combined with that of the flexible aliphatic substituent, is expected to make catalyst approach to the surface difficult. The reason for successful coupling of the surface Si−H groups to the aromatic silanes is certainly related to the large excess of catalyst and aromatic silane with respect to surface Si−H groups; the silane and catalyst molecules are rinsed off upon completion of the reaction, as opposed to solution-phase chemistry. In addition, while undetermined, primary silane groups, $-SiH_3$, do populate the surface, and thus, they may react selectively.

Table 1. Semiqualitative Analysis of Incorporation Levels of Various Silanes on Porous Silicon, as Determined via Integration of the $\nu(\mathrm{Si-H}_x)$ Stretching Region (2000−2200 cm^{-1}) in the FTIR Spectra[a]

Silane				
Incorporation (%)	3±1	8±1	19±4	14±3

[a] $\%E = (A_1 - A_0)/A_0$ where A_1 and A_0 are the final (after reaction) and prior (before reaction) integrated intensities, respectively. The values are the average of three reactions.

To provide complementary information concerning incorporation levels and to yield information concerning the consistency of functionalization into the porous silicon layer, ToF-SIMS has been shown to be useful.[13] The ToF-SIMS analyses are shown for separate porous silicon samples functionalized via zirconocene-catalyzed dehydrocoupling of phenylsilane and 4-fluorophenylsilane and, for comparative purposes, a hydrosilylation reaction of 4-fluorostyrene, a surface reaction that is well established in the literature.[1a,13] As shown in Figure 3, in all the samples, the carbon levels are higher by an order of magnitude than a freshly etched sample of hydrogen-terminated porous silicon and are constant throughout the analysis. In particular for the cases of the similar 4-fluorophenylsilane and 4-fluorostyrene molecules, the carbon and fluorine levels are comparable. The incorporation level of 4-fluorostyrene on a porous silicon surface prepared by $EtAlCl_2$ was determined to be about 13% by FTIR analysis, which is comparable to the 4-fluorophenylsilane molecule, as determined by FTIR (vide supra).

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(23) de Smet, L. C. P. M.; Zuilhof, H.; Sudholter, E. J. R.; Lie, L. H.; Houlton, A.; Horrocks, B. R. *J. Phys. Chem. B.* **2005**, *109*, 12020.

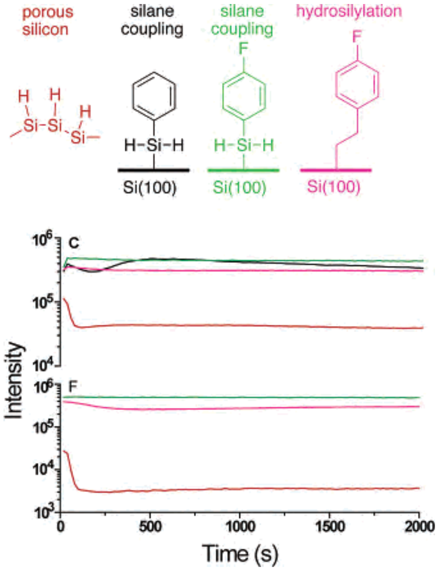

Figure 3. Depth-profiled SIMS of porous silicon surfaces before functionalization (red curves) and after reaction. Top: SIMS showing the level of carbon on surfaces functionalized with phenylsilane (black), 4-fluorophenylsilane (green), and 4-fluorophenethyl (pink) groups. Bottom: the signal level of fluorine in 4-fluorophenylsilane-terminated surface (green) compared to that in a 4-fluorostyrene-reacted surface (pink) and a native, hydride-capped surface (red). As determined by AFM, the depth reached in 2000 s is about 1.5 μm.

At this point, the question that has not yet been touched upon is whether following the coupling of the silane to the surface, subsequent coupling, and hence oligomerization/polymerization leading to polysilane chains on the surface occurs. Due to the intense steric crowding of the Si−H groups of the silane coupled to the surface, it is highly unlikely that they are accessible to the zirconocene catalyst. Indeed, catalyzed dehydrocoupling of two preformed polysilanes remains extremely challenging.[8] Therefore, it is assumed that only one silane can bind to the surface through a Si−Si bond, and no further dehydrocoupling of silanes occurs from this point. Because of the high surface area and corresponding morphological inhomogeneity of porous silicon, it is not possible to experimentally estimate the thickness of the surface layer. On flat silicon surfaces, however, a number of techniques are available. Hydride-terminated Si(100) surfaces were exposed to the zirconocene-catalyzed dehydrogenative coupling conditions in the presence of (separately) the two silanes with the highest incorporation levels, phenylsilane and 4-fluorophenylsilane. As shown by XPS for 4-fluorophenylsilane (Supporting Information) with its readily observable fluorine handle, the expected F 1s peak is observed at 687.4 eV. Little oxidation is noted, based on the Si 2p feature in the same XPS spectrum (Supporting Information). Ellipsometry could provide film thickness information, but because these layers are less than 1 nm thick, this technique is not particularly accurate. AFM tip scribing, on the other hand, now a common technique for removing fragile organic monolayers from hard inorganic surfaces, was used for direct determination of the organic film thickness.[24] Previous work in our group and by others has shown that the pressures applied cause little damage to the underlying silicon.[24a] As shown in Figure 4, removal of the organic layer and imaging of the trough indicates that the interface is about 0.7 nm in thickness, in line with the predicted value (0.7 nm). If the same experiment is carried out in absence of catalyst (with silane only), the measured thickness is about 0.3 nm due to a very thin physisorbed layer of silane and/or hydrocarbon impurities accumulated during the handling, soaking, and rinsing steps. These results suggest that long, higher-molecular-weight silanes growing from the surface are unlikely.

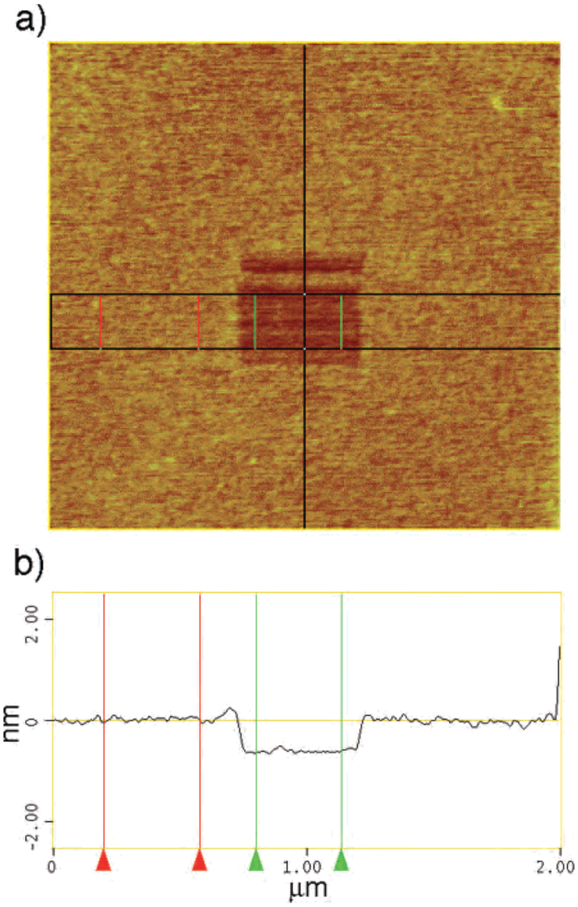

Figure 4. AFM scribing of Si(100) surfaces with functionalized via phenylsilane-coupling prepared by zirconocene catalysis (scan size 2 μm × 2 μm), indicating the film thickness is 0.7 nm thick. The scan force is 130 nN.

To rule out solution-phase polysilane growth and entrapment in the pores of porous silicon or grafting of polysilanes onto the surface, a series of control experiments were carried out; FTIR spectra and additional experimental details are included in the Supporting Information. First, in absence of catalyst, keeping all else identical, the porous silicon is unchanged from the starting native Si−H-terminated surface, as determined by FTIR; neither vibrations associated with any physisorbed or otherwise bound silanes nor oxidation

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were noted. Polysilanes were prepared via dehydrogenative silane coupling using the same zirconocene catalyst and tested for physisorption. Samples of freshly etched porous silicon were soaked for 24 h in 50 μL toluene solutions of polysilanes ($\sim$10 μL of poly(phenyl)-, poly(hexyl)-, and poly(octadecyl)silanes) followed by toluene and ethanol rinsing, and as was observed with the monomeric silanes, the FTIR spectra showed neither incorporation nor oxidation. To ensure that polymerization in the pores was not leading to trapping of unbonded polymer that simply could not escape out of the pores via diffusion, porous silicon samples were terminated with dodecenyl and styrenyl groups prepared through Lewis acid-mediated hydrosilylation.[1c,13a] This chemistry caps all sterically accessible Si−H functionalities, thus eliminating the surface hydrides through which the dehydrocoupling reaction could take place. The remaining $\sim$70% hydrides are far too hindered to undergo substitution. When the styrenyl-terminated surface was exposed to the same catalytic zirconocene conditions as described here with octadecylsilane, no increase in the $\nu(\mathrm{CH}_x)$ was observed. Conversely, a dodecenyl-terminated porous silicon surface[1c,13a] was exposed to the catalytic zirconocene conditions with phenylsilane, and the characteristic aromatic ν(C=C) breathing mode at 1429 cm^{-1} did not appear in the FTIR spectrum. These two experiments suggest that polysilane entrapment in the pores is unlikely, no doubt due to the fact that these polymers are reported to be quite short (10−20 Si atoms).[8a] A final set of control experiments looked at the ability of the zirconocene catalyst to graft presynthesized polysilanes to the hydride-terminated porous silicon. The lack of incorporation of the polysilane, as determined by FTIR, is to be expected since this catalyst system is extremely sensitive to sterics and is inactive toward chain−chain coupling.[8] The sterics of the surface are similar to, if not worse, than a polysilane chain, preventing coupling of the polysilane to the porous silicon surface directly.

Conclusions

Early transition metal complex zirconocene-based catalyzed reactions that are known to be highly reactive for the dehydrogenative coupling of trihydrosilanes, leading to Si−Si bond formation, were applied to hydrogen-terminated silicon surfaces. Heterocoupling of the Si−H group and a molecular silane resulted in formation of a new Si−Si bond that did not appear to undergo further coupling to form covalently bonded polysilane oligomers or polymers, certainly due to steric hindrance. Trihydro arylsilanes showed higher incorporation levels than the corresponding alkylsilanes. The reaction is applicable to both porous silicon and flat silicon surfaces. Compared to the more commonly examined alkene/alkyne surface hydrosilylation reaction, this dehydrogenative silane coupling reaction increases the $\nu(\mathrm{SiH}_x)$ intensity on the porous silicon surfaces. New approaches being investigated include the direct, uncatalyzed reaction of highly reactive silicon derivatives, such as silylenes and other species. This work opens up new avenues into further exploring silicon surface reactivity via wet chemical approaches.

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Supporting Information Available: FTIR, XPS, and AFM spectra/images of control experiments and other interfaces prepared. This material is available free of charge via the Internet at http://pubs.acs.org.

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