New synthetic routes to alkyl monolayers on the Si(111) surface

Boukherroub, R.; Morin, S.; Bensebaa, F.; Wayner, D. D. M.

Publisher's version / Version de l'éditeur:
https://doi.org/10.1021/1a9901478
Langmuir, 15, 13, pp. 3831-3835, 1999

Langmuir

Research Article

New Synthetic Routes to Alkyl Monolayers on the Si(111) Surface

R. Boukherroub, S. Morin, F. Bensebaa, and D. D. M. Wayner

Langmuir, **1999**, 15 (11), 3831-3835• DOI: 10.1021/la9901478 • Publication Date (Web): 06 May 1999

New Synthetic Routes to Alkyl Monolayers on the Si(111) Surface[1]

R. Boukherroub, S. Morin, F. Bensebaa,† and D. D. M. Wayner*

Steacie Institute for Molecular Sciences and Institute for Chemical Process and Environmental Technologies, National Research Council of Canada, Ottawa, Ontario K1A 0R6, Canada

Received February 11, 1999

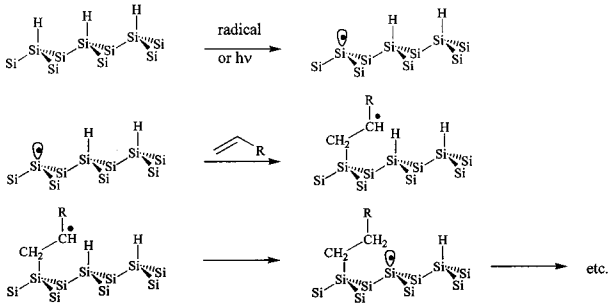
Two new methods for the formation of Si−C monolayers from reactions with Si(111)−H are reported. Besides the photochemical method previously reported by Chidsey, Lewis acid-catalyzed hydrosilylation of alkenes and direct reaction of alkylmagnesium bromide produce a surface with similar chemical composition. These processes are demonstrated and compared using reactions of a C_{10} precursor. The surfaces are chemically stable and can be stored for several weeks without measurable deterioration. The availability of a variety of synthetic approaches leading to the same chemical product is key to the development of flexible surface synthetic strategies. It is expected that these approaches will underpin the development of stepwise solid-phase-like syntheses of more complex organic/bioorganic species on these surfaces.

Introduction

The covalent attachment of organic monolayers to semiconductor surfaces provides a route to passivation and a method to incorporate chemical and biochemical function into solid-state devices. One of the most promising recent advances is based on the seminal work of Chidsey[2−5] in which close-packed monolayers were formed by the reaction of alkenes with hydrogen-terminated Si(111). These reactions were carried out in the neat deoxygenated alkenes using either free radical initiation or ultraviolet irradiation. A simple mechanism was proposed[4] in which radical sites (i.e. dangling bonds), formed by reaction with radicals or by direct irradiation, react with alkenes to form a surface-bonded alkyl radical. This radical in turn abstracts a hydrogen atom from an adjacent Si−H bond, thus saturating the alkyl group and creating another reactive silicon radical. The surface reaction then can proceed as a chain reaction propagated along the surface (Scheme 1). Most recently, Effenberger and co-workers[6] used this approach to photopattern alkenes and aldehydes on silicon surfaces.

Other reaction schemes have been used to generate similarly modified surfaces. Lewis and workers[7] chlorinated the Si(111) surface by reacting the hydrogen-terminated surface with PCl_5 in chlorobenzene at about 80−100 °C. The Si(111)−Cl surface was then reacted with organolithium or Grignard reagents to form the Si(111)−C_nH_{2n+1} surface. The utility of these surfaces as photoanodes was evaluated.[8,9] We have used a similar approach to covalently attach thiophenes to the Si(111) surface.[10] In this case, surfaces were brominated by reaction with *N*-bromosuccinimide or bromotrichloromethane using radical initiating conditions followed by reaction with 2-thienyllithium or the bi- and terthiophene analogues.

Scheme 1



While it may be too early to generalize, it appears that the surface chemistry of Si(111)−H closely parallels molecular organosilane chemistry.[11] We have begun to explore the relationship between the surface chemistry and the known chemistry of simple organosilanes. One of the great strengths and sources of creativity in synthetic organic chemistry is the availability of a number of viable routes to the same chemical product. The same will be true of silicon surface chemistry. A variety of chemical reactions leading to the formation of Si(111)−C bonds will limit functional group incompatibilities and provide opportunities to combine new surface chemical preparations with the well-established solid-phase synthetic and photosynthetic approaches. Such approaches will allow for the incorporation of or stepwise synthesis of more complex organic/bioorganic species on these surfaces. In this work we report two new approaches (as applied to single-crystal surface chemistry) for the formation of alkyl monolayers on Si(111) surfaces. The surfaces are compared to those prepared by photolysis[5] using attenuated total internal reflection (ATR) FTIR, X-ray photoelectron spectroscopy (XPS), and atomic force microscopy (AFM).

† Institute for Chemical Process and Environmental Technologies.

(1) Issued as NRCC Publication Number 40916.

(2) Cicero, R. L.; Wagner, P.; Linford, M. R.; Hawker, C. J.; Waymouth, R. M.; Chidsey, C. E. D. *Polym. Prepr.* **1997**, *38*, 904−905.
(3) Linford, M. R.; Chidsey, C. E. D. *J. Am. Chem. Soc.* **1993**, *115*, 12631−12632.
(4) Linford, M. R.; Fenter, P.; Eisenberger, P. M.; Chidsey, C. E. D. *J. Am. Chem. Soc.* **1995**, *117*, 3145−3155.
(5) Wagner, P.; Nock, S.; Spudich, J. A.; Volkmuth, W. D.; Chu, S.; Cicero, R. L.; Wade, C. P.; Linford, M. R.; Chidsey, C. E. D. *J. Struct. Biol.* **1997**, *119*, 189−201.
(6) Effenberger, F.; Gotz, G.; Bidlingmaier, B.; Wezstein, M. *Angew. Chem., Int. Ed. Engl*. **1998**, *37*, 2462−2464.
(7) Bansal, A.; Li, X.; Lauerman, I.; Lewis, N. S. *J. Am. Chem. Soc.* **1996**, *118*, 7225−7226.
(8) Bansal, A.; Lewis, N. S. *J. Phys. Chem. B* **1998**, *102*, 4058−4060.
(9) Bansal, A.; Lewis, N. S. *J. Phys. Chem. B* **1998**, *102*, 1067−1070.
(10) He, J.; Patitsas, S. N.; Preston, K. F.; Wolkow, R. A.; Wayner, D. D. M. *Chem. Phys. Lett.* **1998**, *286*, 508−514.
(11) Ojima, I. *The Chemistry of Organosilicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: Chichester, U.K., 1989; pp 1479−1526.

10.1021/la9901478
Published on Web 05/06/1999

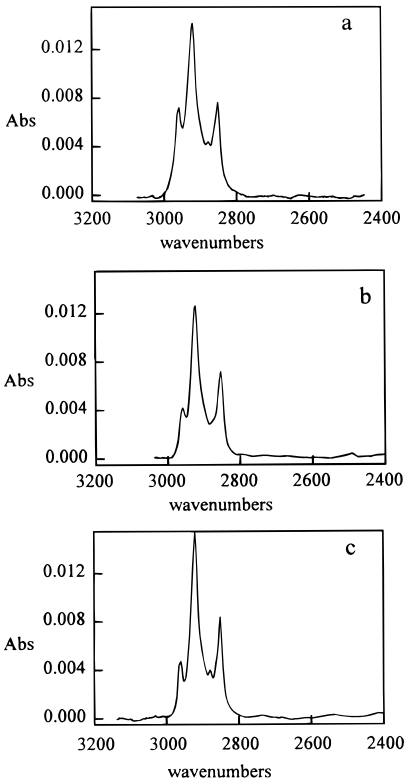


Figure 1. ATR-FTIR spectrum of Si(111)−$C_{10}H_{21}$ prepared by (a) photochemical reaction of decene, (b) catalyzed reaction of decene, and (c) thermal reaction of decylmagnesium bromide with Si(111)−H.

Table 1. Infrared Frequencies and Relative Intensities (Parentheses)[a] of the Asymmetric Methylene Stretch and XP C/Si Ratios of Si(111)−$C_{10}H_{21}$ Prepared by Three Different Reactions of Si(111)−H

method	ν_a, cm^{-1}	C(1s)/Si(2p)[b]
decene + $h\nu$	2922 (1.00)	1.00
decene + $AlEtCl_2$	2923 (0.79)	0.77
decylmagnesium bromide	2920 (0.96)	1.02

[a] Relative to the photochemical preparation. [b] From XPS.

Results and Discussion

Hydrogen-terminated Si(111) was prepared by etching cleaned shards of silicon or silicon ATR elements in 40% ammonium fluoride as described in the literature.[12,13] The infrared absorption at 2083.7 cm^{-1} (p-polarization) together with LEED and XPS confirmed that these surfaces were ideally terminated. AFM and STM imaging showed a surface with atomically flat terraces with monatomic steps approximately 0.32 nm in height. As a starting point we have prepared a decene modified surface using the method described recently by Chidsey.[5] In this case, a shard of Si(111)−H is completely immersed in the neat alkene, deoxygenated by bubbling with argon, and then irradiated. The infrared absorption spectrum of this surface is shown in Figure 1a with the peak positions and relative intensities in Table 1. The absorbance maximum of the asymmetric stretch (0.064 mAbs/methylene) is the same as that for the stable surfaces reported by Chidsey (0.062 mAbs/methylene) when corrections for the different ATR element geometries and the different chain lengths are made. The X-ray photoelectron survey spectrum of this surface (Figure 2a) showed a significant increase in the carbon and oxygen signals compared to those of the hydrogen-terminated surface (Figure 2d). High-resolution XP spectra of the Si(2p) and C(1s) regions (Figure 3a and b) were consistent with a Si−CH_2 bond. The O 1s peak in the survey spectrum does not appear to be associated with the formation of SiO_2 (which would appear at about 102 eV). AFM provided images that resembled those of the hydrogen-terminated surface: atomically flat terraces with monatomic steps (Figure 4a). These surfaces are very stable and can be stored for several weeks without any change in the spectroscopic or topographic properties. AFM is a useful and sensitive tool for the qualitative characterization of the extent and quality of surface reactions. In our experience, when the surface reactions are incom-

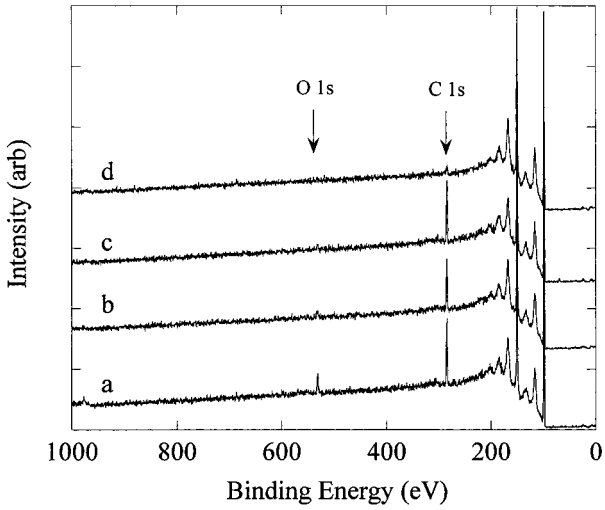


Figure 2. XP survey spectrum of Si(111)−$C_{10}H_{21}$ prepared by (a) photochemical reaction of decene, (b) catalyzed reaction of decene, and (c) thermal reaction of decylmagnesium bromide with Si(111)−H and (d) Si(111)−H. The spectra have been offset for easy viewing.

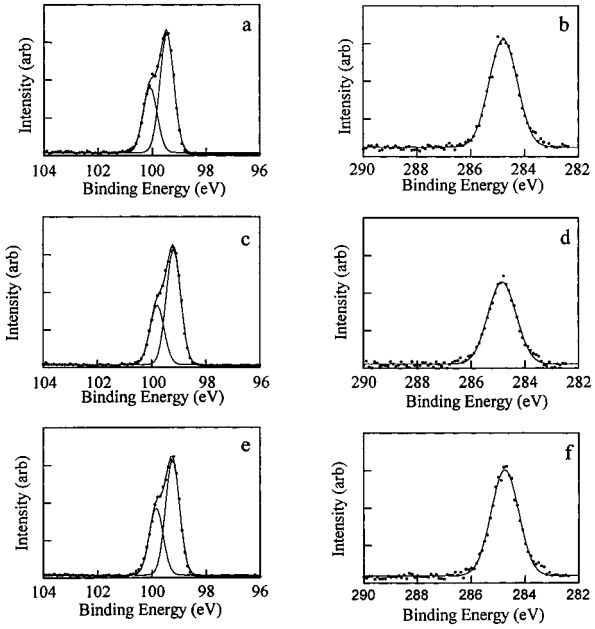


Figure 3. High-resolution XP spectra of surfaces prepared by (a and b) the photochemical reaction of decene, (c and d) the catalyzed reaction of decene, and (e and f) the thermal reaction of decylmagnesium bromide with Si(111)−H. The Si(2p) region is shown in the left column (a, c, and e), and the C(1s) region, in the right column (b, d, and f).

(12) Higashi, G. S.; Chabal, Y. J.; Trucks, G. W.; Raghavachari, K. *Appl. Phys. Lett.* **1990**, *12*, 656.
(13) Wade, C. P.; Chidsey, C. E. D. *Appl. Phys. Lett.* **1998**, *71*, 1679−1681.

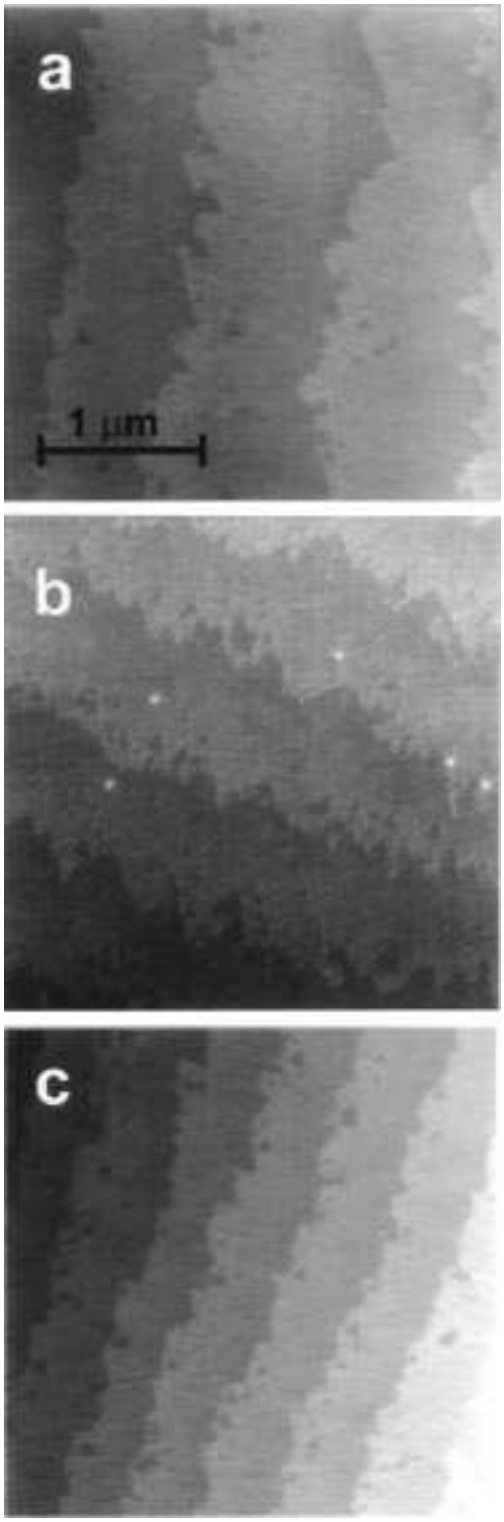
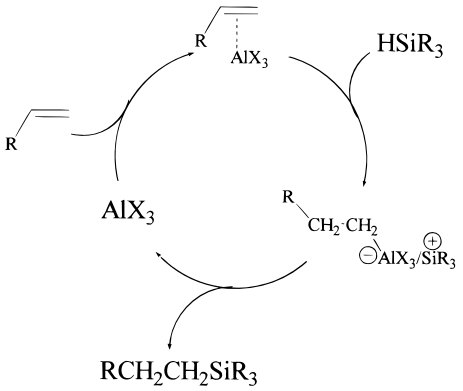


Figure 4. Contact mode AFM images of a 3 μm^2 area of Si-(111)−$C_{10}H_{21}$ prepared by (a) the photochemical reaction of decene, (b) the catalyzed reaction of decene, and (c) the thermal reaction of decylmagnesium bromide with Si(111)−H. The shorter terrace width in part c is due to the use of a different wafer with a slightly different miscut angle.

plete or become contaminated during the reaction or workup, the step edge definition is lost and there is a significant increase in surface roughness. Similarly, the degradation of the surfaces over time can be monitored by AFM by dipping in 2% HF to remove oxidized silicon.

Hydrosilylation of alkenes and alkynes using Lewis acid[14] is well-known in the chemical literature and has

Scheme 2



been applied to the modification of porous silicon.[15] Since these reactions occur under mild conditions and are compatible with a large number of end-group functionalities, it was of interest to see if a catalytic process of this kind could produce a clean alkyl monolayer on the single-crystal surface. The concern, of course, is that the steric demand of the reaction may inhibit simultaneous complexation of the catalyst to the surface and the alkene (Scheme 2). We chose $AlEtCl_2$ as the catalyst for the surface reaction, since it appears to be one of the more effective catalysts for hydrosilylation of triethylsilane. The reaction leads to the incorporation of hydrocarbon on the surface (Figures 1b and 2b). The level of oxygen contamination is very low (Figure 2b). Using the FTIR absorption of the asymmetric methylene stretch (ca. 2920 cm^{-1}), it is possible to determine the relative coverage of alkyl groups (compared to the photochemical reaction). The lower absorption at 2923 in Figure 1b compared to Figure 1a suggests that the hydrocarbon content of the surface modified by the catalytic process is only 0.8 of the surface modified by the photolytic process (Table 1). Similarly, Figures 2b and 3b clearly indicate that the carbon content of the catalytically modified surface is lower as well. The comparison is reasonable, since the level of adventitious carbon contamination is minimal. As a control, the background carbon signal was determined using a freshly terminated Si(111)H surface. As can be seen, the background carbon is only approximately 8% of the total carbon signal of the modified surface (Figure 2d). After correction for the background carbon signal, using Si(111)−H as a standard, the XP data indicate that the fraction of hydrocarbon on the surface also is approximately 0.80 of that obtained by photolysis of the alkene (Table 1). There was no evidence for Al on the surfaces modified using $AlEtCl_2$. These surfaces are still chemically stable and oxide free within the limits of detection of XPS (Figure 2c and d). AFM images of the $AlEtCl_2$-treated surface still show clear terraces and step edges (Figure 3b). The obvious difference between this surface and the photochemically modified surface is the appearance of a small number of clusters with an average diameter of 67 Å and an average height of 15 Å. The composition of these structures, which cover a very small fraction of the surface (ca. 0.002%), is not known at this time. It is interesting that the terraces in Figure 4b appear slightly mottled and roughened compared to those in Figure 4a. This may be associated with the lower coverage.

As a control, the Si(111)−H surface was exposed to the neat alkene at 100 °C for 6 days in the absence of a catalyst.

(14) Asao, N.; Sudo, T.; Yamamoto, Y. *J. Org. Chem.* **1996**, *61*, 7654−7655.
(15) Buriak, J. M.; Allen, M. J. *J. Am. Chem. Soc.* **1998**, *120*, 1339−1340.

Under these conditions, the extent of alkylation of the surface was less than 50% compared to that for the reaction with catalyst after only 18 h. The relative coverage was judged by the intensity of the asymmetric C−H stretching mode, which shifted to 2925 cm^{-1}, indicating a more disordered alkyl layer. Chidsey showed that temperatures near 200 °C are required for the direct thermal reaction.[4]

Our original intention had been to compare the previous two procedures with the reaction of Si(111)−Cl with decylmagesium bromide as described by Lewis and co-workers.[7] In light of the recent report by Kim and Laibinis,[16] in which porous silicon reacted directly with decylmagnesium bromide at room temperature, we carried out a control experiment in which the Grignard reagent was allowed to react directly with the Si(111)−H surface. To our surprise, this reaction is as efficient as the photoreaction of decene, giving an infrared spectrum that has the same asymmetric C−H stretching intensity (Figure 1c, Table 1) with the maximum shifted to a slightly lower frequency. A variation of ±5% reflects the variation in the Si−H stretch intensity that we normally obtain from the etching process. The fact that this reaction occurs is a surprise, since the reaction with porous silicon involves the cleavage of Si−Si back-bonds.[16] It is unlikely that this should occur on the Si(111) surface where the cleavage of a Si−Si bond must lead to a significant increase in strain and must significantly etch the surface. Furthermore, there is no evidence by FTIR of Si−H remaining on the surface.[17] By contrast, the reaction with porous silicon does not appear to lead to the net consumption of hydrogen. Interestingly, the reaction of organolithium reagents is not as efficient as the reactions of the Grignards. The reason for this difference is not clear, and it would be premature to speculate on the mechanism at this time. However, this difference may provide some insight into the mechanism.

X-ray photoelectron spectroscopy of the Grignard modified surfaces suggests a similar total carbon content when compared to the photochemically modified surfaces (Figures 2c and 3e and f and Table 1), again noting that these comparisons are not made on the same sample, so some variation (±5%) is expected. AFM images of these surfaces are similar to those from all of the reactions studied (Figure 4c), showing clear step edges and terraces. These surfaces are not significantly more etched or pitted than surfaces prepared by the photochemical route, again suggesting a different mechanism than in the case of porous silicon (see above). In this case a crystal with a slightly different miscut was used, leading to somewhat narrower terrace widths. Thus, while the mechanism is not yet understood, contrary to what was previously reported,[7] modification of the surface with decylmagnesium bromide does not require a two-step procedure. However, the fact that the direct reaction gives what appears to be a similarly modified surface does not obviate the need to compare the electrochemical properties of these surfaces with those of surfaces modified by the procedure described by Lewis.[7] These comparisons are currently underway.

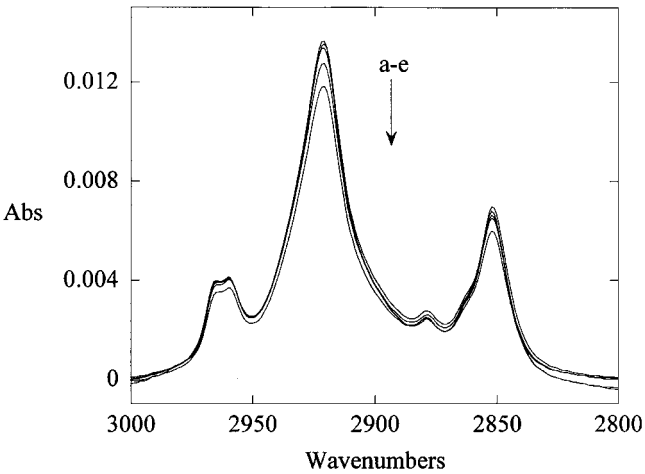


Figure 5. FTIR spectrum of the alkyl C−H stretch region of Si(111)−$C_{10}H_{21}$ prepared by the thermal reaction of decylmagnesium bromide with Si(111)−H: (a) As prepared followed by rinsing with trichloroethane; (b) after sonication for 5 min. in dichloromethane followed by boiling in chloroform for 1 h; (c) after boiling in water for 1 h; (d) after immersion in 40% ammonium fluoride for 10 min followed by 3 days in water; (e) after soaking in 2 M KOH for 10 min.

Chemical Stability of the Surfaces. As pointed out above, the disappearance of the Si−H stretch in the IR is a necessary but insufficient criterion for the formation of a covalently bonded monolayer. There are two reports in the literature which give direct evidence of a Si−C link. Lewis and co-workers[7] used HREELS to characterize the modified surfaces and assigned a peak near 600 cm^{-1} to the Si−C stretch. Chidsey and co-workers used photoelectron diffraction[18] to determine the Si−C bond length. In the absence of direct spectroscopic evidence, chemical robustness is often taken as indirect evidence of a covalent link.[4] In principle, the lack of oxidation of the surface together with the appearance of the alkyl C−H stretch in the IR is also consistent with a physisorbed alkyl layer on the Si(111)H surface. To test the robustness of films, the modified ATR crystals were subjected to the following sequential treatments: (a) sonication in dichloromethane for 5 min, (b) boiling in chloroform for 1 h, (c) boiling in water for 1 h, (d) immersion in 40% deoxygenated ammonium fluoride for 10 min, (e) immersion in MilliQ water for 3 days, (f) immersion in 2 M KOH for 10 min, and (g) immersion in 2 M KOH for 16 h. The results for the surface prepared by the Grignard approach are shown in Figure 5. It is clear that these films are extremely robust. After the first three treatments (Figure 5a−c) the intensity of the asymmetric methylene stretch had dropped by less than 2% (compared to 10−50% as reported by Chidsey and co-workers[4] for surfaces modified by a free radical route). Normally one would expect physisorbed alkanes to be removed by successive washing with trichloroethane, dichloromethane, and chloroform. Treatment with 40% ammonium fluoride (Figure 5d) led to an overall drop of about 8%. Storage of the sample for 3 days in water had no measurable effect on the IR absorption. Finally, immersion in KOH for 10 min led to a further drop of 6%

(16) Kim, N. Y.; Laibinis, P. E. *J. Am. Chem. Soc.* **1998**, *120*, 4516−4517.

(17) It has been suggested by a reviewer that the disappearance of the Si−H stretch at 2084 cm^{-1} does not necessarily imply the formation of Si−C bonds. Partial oxidation of the surface would result in the decrease in the intensity of the Si−H stretch at 2084 cm^{-1} and an increase in peaks at higher frequencies associated with OSi−H at 2120 cm^{-1} up to O_3SiH at 2250 cm^{-1} (Weldon, M.; Stefanov, B. B.; Raghavachari, K.; Chabal, Y. *Phys. Rev. Lett.* **1997**, *79*, 2851). The half-life for disappearance of the Si(111)H stretch is 15 h at a relative humidity of 10% (Miura, T.; Niwano, M.; Shoji, D.; Miyamoto, N. *J. Appl. Phys.* **1996**, *79*, 4373). Under the reaction conditions, the effective humidity is extremely small. It is true that the disappearance of the Si−H stretch is a necessary but insufficient criterion for the formation of a covalent link to the surface. However, partial oxidation of the surface, even a monolayer of oxygen, is readily detectable by XPS. We have found (unpublished data) that the high-resolution XP spectrum of the Si 2p peak of the Si(111)−$OC_{10}H_{21}$ surface must be fit with three Gaussians (Si $2p_{1/2}$, Si $2p_{3/2}$, and a smaller contribution about 0.3 eV higher in binding energy that is assigned to Si−O).

(18) Terry, J.; Linford, M. R.; Wirgen, C.; Cao, R.; Pianetta, P.; Chidsey, C. E. D. *Appl. Phys. Lett.* **1997**, *71*, 1056.

(ca. 13% overall). The KOH treatment is particularly aggressive. After soaking in 2 M KOH for 16 h, all of the hydrocarbon was removed. A similar lack of stability toward strong alkali was reported by Chidsey.[4] The surface prepared by the catalysis route is somewhat less stable. While there was no change after sonication, after boiling in chloroform and water the asymmetric methylene intensity dropped by 6%. After soaking in 40% ammonium fluoride, an additional drop of 12% was observed (17% overall). This is not surprising, since we have shown that the hydrocarbon content of this surface is only 80% of those formed by the photolysis or the Grignard routes. The lower stability and the apparently rougher surface by AFM (Figure 4b) are consistent with a more defect-ridden surface that is exposed to attack by the etchant.

Conclusions

It is possible to produce covalently bonded alkyl monolayers on Si(111) surfaces using a variety of chemical reactions with Si(111)−H. Besides the photochemical method previously reported by Chidsey, Lewis acid-catalyzed hydrosilylation of alkenes and direct reaction of alkylmagnesium bromide produce surfaces with similar characteristics. These surfaces are chemically stable and can be stored for several weeks without measurable deterioration. AFM shows that these surfaces retain their original topographic appearance, having well-defined terraces and steps with little or no apparent contamination on the several micron scale. The availability of several synthetic approaches to the same chemical product is key to the development of flexible surface synthetic strategies. It is expected that these approaches will underpin the development of stepwise solid-phase-like syntheses of more complex organic/bioorganic species on these surfaces.

Experimental Section

Silicon wafers were purchased from Virginia semiconductor. ATR elements ($25 \times 5 \times 1$ mm^3) were purchased from Harrick. All cleaning and etching reagents were clean room grade and were supplied by Amplex. All other reagents were obtained from Aldrich and were the highest purity available.

Hydrogen-terminated Si(111) was prepared from shards of silicon (0.5−5.0 Ω·cm, n-type) by cleaning in 3:1 concentrated H_2SO_4/30% H_2O_2 at 100 °C for 20 min, followed by copious rinsing with MilliQ water. The surfaces were etched with clean room grade 40% aqueous deoxygenated NH_4F (15 min)[13] and transferred, without rinsing, into the reaction vessel. The Si(111) attenuated total internal reflectance (ATR) crystals were cleaned by the standard RCA procedure prior to etching. We found that the RCA clean was more effective when the surfaces were reused many times, as judged by the reproducibility of the Si−H absorption intensity at 2083.7 cm^{-1}.

ATR-FTIR spectra were recorded using a Nicolet MAGNA-IR 860 spectrometer at 2 cm^{-1} resolution. The ATR crystals were mounted in a purged sample chamber with the light focused normal to one of the 45° bevels. Background spectra were obtained using a freshly hydrogenated surface.

Atomic force microscopy was carried out using a Molecular Imaging PicoSPM equipped with an environmental chamber and a Nanoscope IIIa controller (Digital Instruments). The sample was kept in an argon environment for all measurements. AFM images were acquired at 1 Hz in contact mode using silicon nitride-sharpened tips (Digital Instruments. 0.12 N m^{-1}) at a constant force of 1−2 nN. All images are leveled but otherwise unfiltered.

X-ray photoelectron spectra (XPS) were recorded on a Kratos Axis Instrument, using monochromated Al Kα (1486 eV) radiation with detection on the surface normal. The pressure during analysis was about 5×10^{-8} Torr.

Reaction of Si(111)H with Decene by the Photochemical Route.[2] A freshly hydrogen-terminated surface was transferred under argon, into a Schlenk tube containing 10 mL of deoxygenated 1-decene, and irradiated in a Rayonet reactor (300 nm) for 5.5 h. The functionalized substrate was rinsed with pentane, MilliQ water, and trichloroethane.

Reaction of Si(111)H with Decene by the Catalytic Route. As above, the freshly hydrogen-terminated surface in a Schlenk tube containing 10 mL of deoxygenated 1-decene and 1 mL of 1.0 M ethylaluminum dichloride ($EtAlCl_2$) in hexane was allowed to react for 18 h at 100 °C. The excess of unreacted 1-decene and $EtAlCl_2$ was removed by rinsing with THF, water, and trichloroethane at room temperature.

Reaction of Si(111)H with Decylmagnesium Bromide. The freshly hydrogen-terminated surface in a Schlenk tube containing 10 mL of deoxygenated decylmagnesium bromide (1.0 M solution in diethyl ether) was warmed for 16 h in a constant-temperature bath set to 85 °C. The actual temperature of the reaction was not measured; however, the volume of the liquid did not change and there was no apparent refluxing. The silicon substrate was then rinsed at room temperature with 1% CF_3COOH solution in THF, MilliQ water, and finally trichloroethane.

LA9901478