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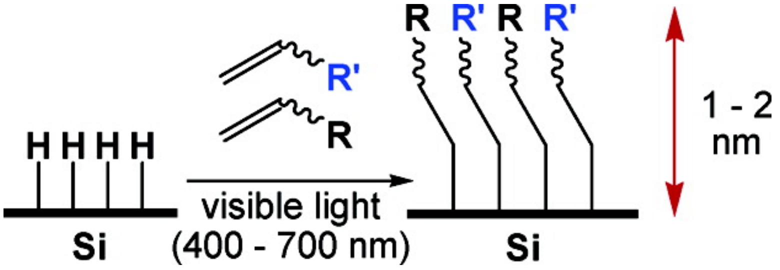

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Covalently Attached Monolayers on Crystalline Hydrogen-Terminated Silicon: Extremely Mild Attachment by Visible Light

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Abstract: A very mild method was developed for the attachment of high-quality organic monolayers on crystalline silicon surfaces. By using visible light sources, from 447 to 658 nm, a variety of 1-alkenes and 1-alkynes were attached to hydrogen-terminated Si(100) and Si(111) surfaces at room temperature. The presence and the quality of the monolayers were evaluated by static water contact angles, X-ray photoelectron spectroscopy, and IR spectroscopy. Monolayers prepared by thermal, UV light, or visible light initiation were compared. Additionally, the ability of infrared reflection−absorption spectroscopy to study organic monolayers on silicon was explored. A reaction mechanism is discussed on the basis of investigations of the reaction behavior of 1-alkenes with silicon wafers with varying types and levels of doping. Finally, a series of mixed monolayers derived from the mixed solutions of a 1-alkene and an ω-fluoro-1-alkene were investigated to reveal that the composition of the mixed monolayers was directly proportional to the molar ratio of the two compounds in the solutions.

Introduction

Over the past eight to ten years several methods have been developed to prepare organic monolayers on various morphologies of hydrogen-terminated silicon.[1−3] Si−C bond attached monolayers have been prepared by making use of thermal conditions,[4−8] UV irradiation,[9−12] electrochemistry,[13−15] hydrosilylation catalysts,[16−19] and chemomechanical scribing.[20−22] These studies have allowed a proper characterization of such monolayers, and now allow a focus on the integration of functional groups or biomolecules in monolayers on the silicon surface. Although thermal conditions and UV irradiation yield stable[5,6] and densely packed monolayers,[7,23] they are too harsh to allow the use of labile bioactive materials. This situation has two ways out (Scheme 1). In the first route (route 1) one makes use of a protected precursor that can stand such harsh conditions (1a). Subsequently, this precursor is deprotected (1b) and

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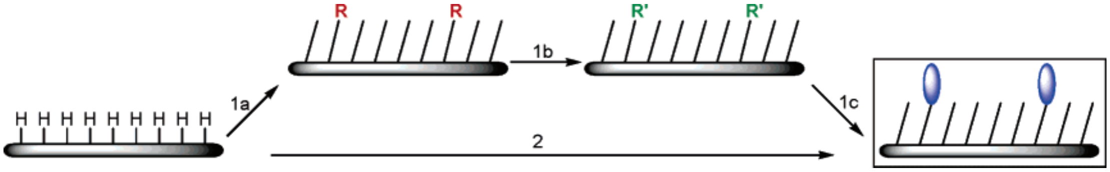
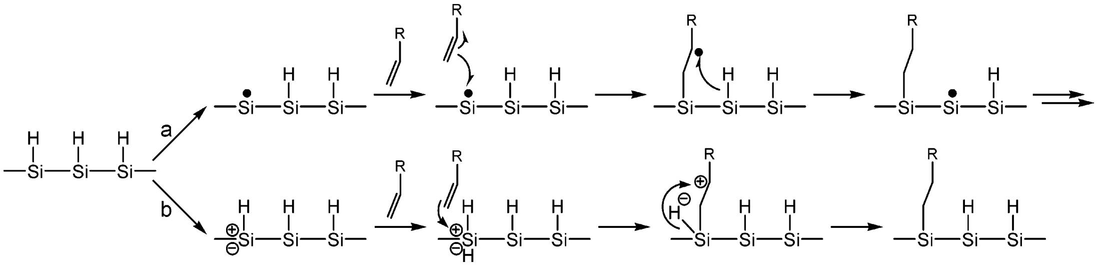
Scheme 1. Preparation of Mixed Monolayers (Box) Containing Biomolecules (Oval Symbols) via Indirect (1) or Direct (2) Methods[a]



[a] See the text.

Scheme 2. Representation of the Proposed (a) Radical Chain Mechanism[5] under Thermal and UV Conditions and (b) Electron/Hole Pair Mechanism[28] for Visible-Light-Initiated Hydrosilylation on Porous Silicon



transformed (1c) into the bioactive monolayer. Such an approach has been taken by, e.g., the groups of Hamers,[12,24] Horrocks and Houlton,[25,26] and Wei et al.[27]

The second route (2) would make use of mild reaction conditions that are compatible with bioactive moieties. In the case of porous silicon such an approach might be possible on the basis of the white-light-promoted reaction discovered by Stewart and Buriak.[28] It was demonstrated that excitons generated through illumination of the surface of photoluminescent porous silicon with white light (≥400 nm) are capable of driving a surface hydrosilylation reaction on hydride-terminated porous silicon, producing Si−C bonds, also in line with recent computational studies.[29] On the basis of the bond strength of the Si−H bond, a minimum energy of 3.5 eV ($\lambda < 350$ nm) is required to perform Si−H bond cleavage. Since Stewart and Buriak used wavelengths ≥400 nm, they concluded that the mechanism of hydrosilylation on porous silicon does not start with a homolytic cleavage of the Si−H bonds. For this reason a radical chain mechanism[5] (Scheme 2, top), as operative in the case of thermal and UV hydrosilylation, was rejected, and a new mechanism was proposed that involves attack by a 1-alkene or 1-alkyne on a surface-localized positive charge (the hole) in a nucleophilic fashion, resulting in Si−C bond formation (Scheme 2, bottom).[28] It was thought that quantum confinement effects were crucial for this attachment reaction, which was thus thought to be limited to porous silicon. This was in line with observations by Effenberger and co-workers,[10] who used 380 nm light for the modification of flat hydrogen-terminated Si(111) with 1-octadecene, but the reported water contact angles (only ∼95°) indicated a poor monolayer quality. To circumvent this limitation, Hamers studied partially iodinated Si(111) and Si(100) surfaces, and reported visible light (514 nm) initiated modification thereof.[30] This reaction works well, but requires an extra step, and involves a somewhat poorly defined substrate due to the fact that the iodination is only partial.

Therefore, we were motivated to find an easy and extremely mild route to modify planar Si surfaces, and recently, we introduced this via the use of visible light (447 nm) to attach organic monolayers on flat hydrogen-terminated silicon surfaces.[31] Angle-resolved X-ray photoelectron spectroscopy (ARXPS), infrared spectroscopy, and contact angle measurements were used to show the formation of densely packed monolayers. In another paper, we demonstrated the potential of this reaction, by the attachment of a fragile monosaccharide.[32] However, no systematic study has as yet been reported on the influence of the nature and degree of doping, the variation of the irradiation wavelength, and the type of silicon surface [Si(100) vs Si(111)]. In addition, no detailed surface studies by scanning force techniques and X-ray reflectivity measurements have yet been made, nor a fully unambiguous comparison between the thermal and this new photochemical method regarding the obtainable density of the resulting monolayers. Finally, no systematic evaluation has yet been undertaken on the applicability of IRRAS (infrared reflection−absorption spectroscopy) measurements in the analysis of organic monolayers. Such an evaluation would be highly useful, given the ease of use of this technique in the analysis of organic monolayers, as recently shown by us in a study of organic monolayers covalently attached to silicon nitride surfaces.[33] In the present paper we aim to address these issues and in combination with our earlier work try to develop an overall picture of the scope of this mild attachment reaction.

Experimental Section

Materials. (a) Chemicals. PE40/60, MeOH, EtOH, and CH_2Cl_2 were distilled prior to use. Distilled CH_2Cl_2—used as a solvent in chemical reactions—and acetonitrile were distilled over CaH_2 prior to

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use. Mesitylene (Fluka, 99%) was distilled and stored on $CaCl_2$. The dried mesitylene was filtered to remove traces of $CaCl_2$. 1-Decene (Fluka, 97%) and 1-hexadecene (Sigma, ∼99%) were distilled at least twice at reduced pressure. Triethylamine (TEA; Acros, 99%) was dried over KOH. 1-Docosene (TCI America, 99+%), 10-undecen-1-ol (Aldrich, 98%), acetone (Acros, 99+%), methanesulfonyl chloride (Janssen Chimica, 99%), KF (Jansen Chimica, p.a.), and 18-crown-6 (Acros, 99%) were used as received. HF (Fluka, 50% p.a.-plus) was diluted with demineralized H_2O. 10-Undecenoic acid methyl ester was prepared and purified as described earlier.[6] All reactions were performed under a nitrogen atmosphere. Straight-chain alkanes for the IRRAS calibration were obtained from Aldrich (99+% purity).

(b) Wafers. Single-polished Si(100): n-type, 500−550 μm thick, resistivity 1−2 Ω cm (Seltec Silicon, Mitsubishi Silicon America); p-type, 375 μm thick, resistivity 1−2 Ω cm (Bayer Solar Freiberg, Germany); n-type, 500−550 μm thick, resistivity 0.008−0.02 Ω cm; p-type, 500−550 μm thick, 0.01−0.02 Ω cm (Addison Engineering, San Jose). Single-polished Si(111): n-type, 475−550 μm thick, resistivity 1−5 Ω cm (Addison Engineering, CA); p-type, 500−550 μm thick, resistivity 0.009−0.012 Ω cm (Addison Engineering). In this paper silicon with resistivities of 1−5 and 0.008−0.02 Ω cm is referred to as lowly doped and highly doped, respectively. Lowly doped n-type Si(100) was used throughout this paper, unless specifically noted otherwise.

Purification and Analysis of Synthesized Compounds. Thin-layer chromatography (TLC) was performed on Merck silica gel 60F254 plastic sheets, and detection was realized by charring with an aqueous solution of $KMnO_4$. Column chromatography was conducted by elution of a column of Merck Kieselgel silica (230−400 mesh) using eluents as specified below. NMR spectra were recorded on a Bruker AC-E 400 spectrometer in $CDCl_3$ (dried over Al_2O_3) at room temperature. Gas chromatography (GC) measurements were performed on a Hewlett-Packard 5890 series II chromatograph that was equipped with a DB-17 column and an FID detector. GC samples were dissolved in ethyl acetate or diethyl ether.

Synthesis of 11-Fluoro-1-undecene. 10-Undecen-1-ol (8.501 g, 49.92 mmol) was dissolved in 65 mL of dry CH_2Cl_2, and 10.4 mL (7.59 g, 75 mmol) of triethylamine was added. The stirred solution was cooled to −10 °C, and 8.6 g (75 mmol) of mesyl chloride in 20 mL of dry CH_2Cl_2 was added dropwise at such a rate that the temperature of the solution was not higher than 0 °C. Thirty minutes after the addition was accomplished, TLC (PE40/60:CH_2Cl_2 = 1:4) showed that hardly any starting material ($R_f = 0.17$) was left, and a product with $R_f = \sim 0.38$ was formed. The solution was stored at −35 °C until further workup. The yellow suspension was washed with 200 mL of 0.5 M HCl and the product extracted with CH_2Cl_2 (5 × 75 mL). The combined organic layers were washed with saturated $NaHCO_3$ (3×) and dried over Na_2SO_4. After filtration the solvent was removed under a reduced pressure, yielding 12.786 g of crude product. TLC and ^{1}H NMR showed that 10-undecenyl mesylate was pure enough for further use.

KF (5.8 g, 100 mmol) and 18-crown-6 (26.4 g, 100 mmol) were dissolved in acetonitrile (50 mL). The solution was heated to 60 °C, and to the resulting white suspension was added 12.394 g (49.9 mmol) of 10-undecenyl mesylate dissolved in 50 mL of acetonitrile over a period of 45 min. Subsequently, the solution was refluxed overnight. The course of the reaction was followed by TLC and ^{1}H NMR via the workup of small analytical samples. After 20 h, ^{1}H NMR showed that about 60% of the 10-undecenyl mesylate was still present, and therefore, 1 equiv of KF and 18-crown-6 were added to the reaction mixture. After another 20 h, TLC and ^{1}H NMR showed that most of the starting material had disappeared. The solvent was removed under a reduced pressure. PE40/60 (200 mL) and water (100 mL) were added to the mixture. The organic layer was separated, and the water layer was washed twice with PE40/60 (100 mL). The combined organic layers were washed with brine (300 mL) and dried over Na_2SO_4. After filtration, evaporation yielded 7.228 g of crude product. Column chromatography (PE40/60 as eluent) yielded 4.173 g (24 mmol, 48%) of 11-fluoro-1-undecene: TLC R_f(PE40/60:CH_2Cl_2 = 1:4) = 0.81 and R_f(PE40/60) = 0.44; GC R_t(115 °C) = 6.8 min; ^{1}H NMR δ = 5.88−5.78 (m, 1H), 5.04−4.94 (m, 2H), 4.51 and 4.39 (dt, 2H, J = 47.2 Hz, J = ∼6.2 Hz), 2.10−2.05 (q, 2H, J = ∼6.8 Hz), 1.77−1.65 (m, 2H), and 1.42−1.37 (m) and 1.33 (br s, 12H); ^{13}C NMR δ = 139.45, 114.48, 85.22, and 83.59 (J = 163.5 Hz), 34.21, 30.93, and 30.74 (J = 19.3 Hz), and 29.88, 29.80, 29.64, 29.51, 28.33, 25.59, and 25.54 (J = 5.4 Hz); MS m/z 172.1622 (calcd for $C_{11}H_{21}F$, 172.1627).

Sample Cleaning and Etching. Si samples were first wiped with a tissue that was saturated with chemically pure acetone. After that, the samples were sonicated for at least 10 min in acetone. Then the samples were placed in an oxygen plasma cleaner (Harrick PDC-32G) for 10 min. Subsequently, the Si(100) samples were etched in 2.5% aqueous HF for 2 min, while Si(111) samples were etched in an argon-saturated 40% aqueous NH_4F solution for 15 min under an argon atmosphere. To recycle the relatively expensive attenuated total reflection (ATR) crystals, they were cleaned by oxidative removal of a previously formed monolayer in "piranha solution" (30% H_2O_2:H_2SO_4 = 1:2 (v/v)) at 85 °C for 1 h (*caution: piranha solutions should be handled with great care*),[8] and subsequently etched with HF as described above.

Monolayer Preparation. (a) Photochemical Method. A solution (1.5−3 mL, 0.1−0.5 M) of 1-alkene(s) in mesitylene was flushed with argon for at least 30 min before the freshly etched hydrogen-terminated Si sample was added. After that, the solution was flushed for another 30 min. Then, the argon inlet was moved to a position just above the solution to change from a bubbling solution to a decent gas flow. After that, the lamp—in all cases fixed at a distance of 0.5 cm from the reaction vessel—was turned on. For the modification of ATR crystals two lamps were used. The setup was covered with aluminum foil. Depending on the wavelength, different vessels with a rectangular bottom part were used (quartz vessel for 254 nm and conventional glassware for all other wavelengths). After illumination for the desired time, the sample was removed from the solution, and the surface was excessively rinsed with PE40/60, EtOH, and CH_2Cl_2, respectively. The following models of double-bore lamps were obtained from Jelight Co. Inc. (Irvine, CA): 82-3309-2 (254 nm), 84-2051-2 (371 ± 19 nm = width at half of the maximum intensity), 84-247-2 (447 ± 32 nm), 84-213-2 (504 ± 30 nm), and 84-236-1 (658 ± 14 nm).

(b) Thermal Method. A solution (8.5 mL, 0.2 M) of 1-alkene(s) in mesitylene was placed in a small three-necked flask fitted with a nitrogen inlet, a reflux condenser with a $CaCl_2$ tube, and a stopper. The solution was refluxed for at least 45 min under a flow of nitrogen. Subsequently, a cleaned and freshly etched sample was added to the refluxing solution, while a slow nitrogen flow was maintained. After 2 h the modified sample was removed from the solution and excessively rinsed with PE40/60, EtOH, and CH_2Cl_2, respectively.

Analysis of the Monolayers. (a) Contact Angle Measurements. In all cases where modified samples were analyzed by different techniques a small piece (∼5 mm × 10 mm) was cut from the sample directly after cleaning. Static water contact angles were obtained using an Erma G-1 contact angle meter (volume of the drop of ultrapure water, 3.5 μL). Contact angles of two or three drops were measured. The error of the contact angles is ±1°.

(b) IRRAS. FT infrared reflection−absorption spectra were recorded on a Bruker Tensor 27 instrument equipped with a variable-angle reflection Auto Seagull accessory. A Harrick grid polarizer was installed in front of the detector for measuring spectra with p-polarized (parallel) radiation with respect to the plane of incidence at the sample surface. Single-channel transmittance spectra (4096 scans) were collected using a spectral resolution of 4 cm^{-1}. All (data derived from) spectra shown in this paper are a result of spectral subtraction of modified samples with a cleaned native oxide-covered silicon sample without any further data manipulation.

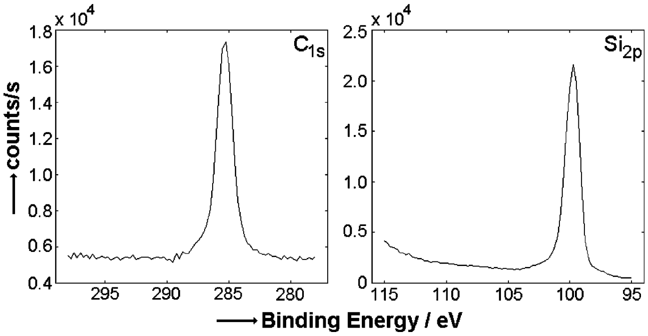

Figure 1. C_{1s} and Si_{2p} regions of an XPS spectrum of an *n*-hexadecyl monolayer on Si(100) prepared via the visible light method (447 nm, 15 h).

Table 1. Static Water Contact Angles (deg) of Monolayers on Silicon Surfaces Prepared by 447 nm Irradiation and Thermal Methods[a]

reactant	447 nm, Si(100)	447 nm, Si(111)	thermal, Si(100)
$CH\equiv CC_{10}H_{21}$	108	109	108[b]
$CH\equiv CC_{12}H_{25}$	110	110	110[b]
$CH\equiv CC_{14}H_{29}$	110	110	110[b]
$CH_2{=}CHC_{10}H_{21}$	109	109	108[c]
$CH_2{=}CHC_{12}H_{25}$	108	110	108[c]
$CH_2{=}CHC_{14}H_{29}$	109	110	109[c]
$CH_2{=}CHC_8H_{16}COOCH_3$ (**I**)	78	75	77[c]
$CH_2{=}CHC_8H_{16}COOCH_2CF_3$ (**II**)	85	86	88[d]

[a] Conditions: irradiation method, 15 h, room temperature; thermal method, heating in a neat reactant[6] or refluxing for 2 h in a 0.2 M solution in mesitylene.[8] All experiments were performed at least twice, experimental error ±1°. [b] From ref 8. [c] From ref 6. [d] Newly obtained using conditions as described in ref 8.

(c) XPS. XPS measurements were performed on a VG Ionex system equipped with a Clam II analyzer and a standard Al Kα X-ray source. Spectra were taken in normal emission at 10^{-9} mbar within 10 min. All C_{1s} peaks corresponding to hydrocarbons were calibrated to a binding energy of 285.0 eV to correct for the energy shift caused by charging. The XPS measurements for Figure 1 were performed on a Quantera SXM from Physical Electronics, equipped with a monochromator and an Al Kα X-ray source of 1486.6 eV. The spot was 100 μm in diameter.

(d) X-ray Reflectivity. X-ray reflectivity measurements were performed on a Panalytical X'Pert Pro diffractometer using Cu Kα radiation (tube settings 40 kV and 40 mA). The data were collected using a fixed divergence slit of 1/32° and a parallel plate collimator on the diffracted beam side. The layer thickness is calculated from the interference fringes. The error in the measurement is depicted as the standard deviation of five measurements on the same sample.

(e) Atomic Force Microscopy (AFM). Surface topography was imaged using a Nanoscope III atomic force microscope (AFM Digital Instruments, Santa Barbara, CA). The contact mode (CM-AFM) with silicon nitride cantilevers (Digital Instruments) with a spring constant of about 0.58 N/m was used.

Results and Discussion

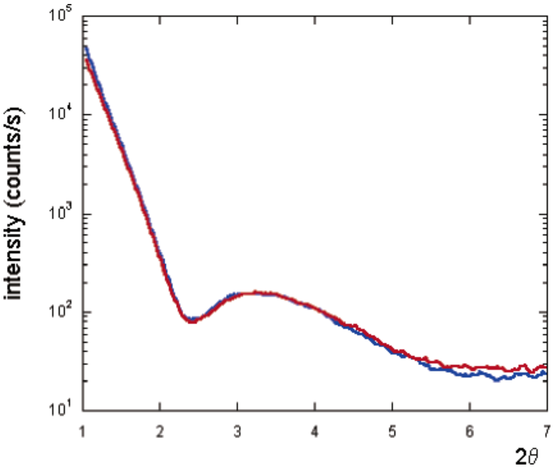

Figure 2. X-ray reflectivity profiles for *n*-docosyl monolayers on lowly doped n-Si(100) prepared via the thermal (red) and visible light (447 nm, 15 h, blue) methods.

Formation of Organic Monolayers on Si(100) and Si(111) Using 447 nm Light. Table 1 lists the static water contact angles of the Si(100) and Si(111) surfaces modified by a variety of 1-alkenes and 1-alkynes and two esterified-1-alkenes (compounds **I** and **II**) using 447 nm light (15 h). The work on monolayers on Si(100) was communicated previously,[31] where it was shown that the monolayer formation was complete after 10 h. The contact angles of the nonfunctionalized monolayers indicate a high hydrophobicity, and the values are comparable with those of high-quality monolayers prepared under thermal conditions.[8] The contact angles of monolayers of compounds **I** and **II** are lower due to the presence of the polar functionality, and in both cases comparable to those of monolayers prepared via thermal methods. Finally, the differences between the contact angles of monolayers of **I** and **II** on Si(100) and Si(111) are small, which indicates that after monolayer formation the top of the organic monolayer does not obviously "display" the character of the silicon substrate anymore. These initial characterizations drove us to more detailed investigations using XPS, X-ray reflectivity, and AFM.

Visible-light-prepared (447 nm) hexadecyl monolayers on Si(100) were analyzed by XPS, a very useful tool for the study of covalently attached monolayers on silicon.[9,12,16,24,30,34−41] Figure 1 shows the C_{1s} and Si_{2p} regions of the XPS spectrum of a monolayer derived from 1-hexadecene on hydrogen-terminated Si(100). The C_{1s} region spectrum shows a clear peak at 288 eV that is absent on samples without a monolayer, supporting the formation of covalently attached monolayers. In addition, the Si_{2p} spectra display hardly any contribution of Si−O bonds (103−104 eV), indicating there is only a small amount of surface oxidation observable.

X-ray reflectivity measurements were performed to compare *n*-docosyl (*n*-$C_{22}H_{45}$) monolayers on Si(100) prepared via either visible light or thermal attachment methods. 1-Docosene was chosen as the alkene, since this yielded a monolayer with sufficient thickness to obtain quantitatively reliable X-ray reflectivity data. Figure 2 shows the X-ray reflectivity profiles for two monolayers obtained by 447 nm irradiation or thermal treatment, respectively. Just like the static water contact angles of these layers (∼107°), the X-ray reflectivity profiles are almost

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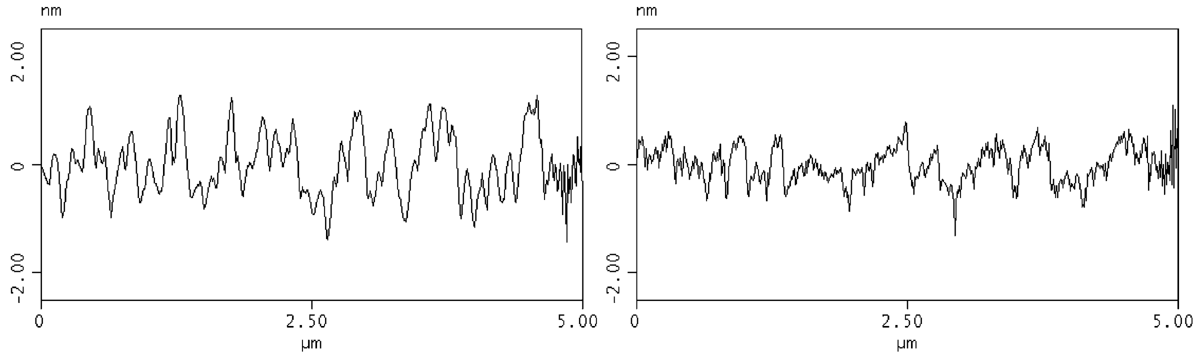

Figure 3. Section analysis obtained via contact mode AFM of photochemically prepared *n*-hexadecyl-modified Si(100) (left) and Si(111) (right) wafers [447 nm, 15 and 5 h, respectively].

Table 2. Static Water Contact Angles (deg) of 1-Hexadecene-Derived Monolayers on Lowly Doped n-Type Si(100) (15 h of Irradiation) and Lowly Doped n-Type Si(111) (5 h of Irradiation) Prepared by Different Wavelengths

λ (nm)	n-type Si(100)	n-type Si(111)	λ (nm)	n-type Si(100)	n-type Si(111)
254	109	110	504	108	110
371	109	110	658	108	110
447	109	109			

identical. The monolayer thickness obtained from the X-ray data is 26 ± 1 Å for both monolayers. Using the calculated length of an *all-trans*-docosyl tail (27.9 Å),[42] the tilt angle with respect to the normal of the surface can be calculated. This results in a tilt angle of 15−26°, of which the top limit is close to the tilt angles of thinner alkyl monolayers.[6]

Monolayers of 1-hexadecene on Si(100) and Si(111)—prepared via the thermal and visible-light methods (447 nm)—were evaluated using CM-AFM. In Figure 3 the corresponding section analyses are presented for the photochemically prepared samples. CM-AFM shows that after wet etching and monolayer formation flat surfaces can be maintained, and no significant differences were observed between thermally and photochemically prepared samples. In addition, the modified Si(111) surface (Figure 3, right) remains a bit more smooth than the Si(100) surface (Figure 3, left). The observed flatness is of the same order of magnitude as reported recently by Cattaruzza et al. for the thermal functionalization of H-terminated Si(100) with 6-heptynoic acid methyl ester.[43] In addition, Wayner and coworkers used AFM to study decyl-modified Si(111) surfaces prepared via different techniques, and reported atomically flat terraces.[16]

Effect of Irradiation Wavelength. The possibility to achieve monolayer attachment even under milder conditions was tested via the study of the photochemical reaction over a wide range of wavelengths (254−658 nm, Table 2) using phosphorescent lamps with various emission maxima (see the Experimental Section), and via the use of a wide-spectrum fluorescent lamp in combination with the appropriate wavelength filters. The maximum contact angles of an *n*-hexadecyl monolayer that can be achieved using light of 371 nm to up to at least 658 nm on both H-terminated Si(100) and Si(111) are comparable with that of high-quality monolayers prepared by UV light (254 nm) or thermal initiation reaction, ∼108−110°. This indicates the possibility to obtain densely packed monolayers under a wide range of mild conditions and the resulting compatibility with biomaterials, one example of which can be found in the direct attachment of labile sialic acid derivatives that have limited stability at high temperature.[32]

The easiest way to obtain fully covered modified Si wafers is to use cheap wide-spectrum phosphorescent “high-efficiency” lamps, possibly in combination with appropriate wavelength filters. Broad-spectrum (15 W, 400−730 nm) lamps, in combination with light filters that remove all light below 500, 550, or 600 nm, yielded *n*-hexadecyl monolayers with a contact angle of ≥108° upon irradiation for 14 h. The quality of the monolayer seems to be dependent more on the humidity of the surroundings and the completeness of oxygen removal than on the precise light source used.

Upon irradiation with UV light (254 nm) the color of a 1-alkene in mesitylene solution becomes yellow, indicating the photochemical formation of side products.[44] The use of visible light of 371−658 nm did not result in a color change. Gas chromatography experiments indeed showed the formation of additional products after irradiation with UV light, while the composition of the solution did not change detectably upon irradiation with 447 nm light. The (likely almost) unchanged nature of alkene/mesitylene solutions after 371−658 nm irradiation allows the use of recycled alkene/mesitylene mixtures after minimal purification efforts (washing the complete solution through a small silica plug to remove trace amounts of any polymers), which is specifically advantageous in light of the synthetic efforts that are sometimes required to obtain functionalized alkenes.

One of the most versatile functional groups to have available on the surface would be the carboxylic acid moiety. In the thermal reaction this can only be obtained via the use of, e.g., esters,[6,12,24,45,46] as the direct attachment of compounds with free hydroxyl moieties yields undesirable reactivity of those functional groups, leading to Si−O(CO)R bond formation. Hydrolysis of the ester, e.g., by treatment with potassium *tert*-butoxide in DMSO, then yields carboxylic acid-modified monolayers with contact angles of ∼52°.[12] However, recently, Liu et al. showed that this deprotection method diminishes the amount of attached alkyl tails in the monolayer.[45] Interestingly, Wayner and coworkers recently reported ATR spectra of monolayers of undecenylic acid on hydrogen-terminated Si(111), which were

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[42] This value was obtained via a semiempirical calculation (MOPAC, PM3, closed-shell-restricted) in Chem3D Pro.

[43] Cattaruzza, F.; Cricenti, A.; Flamini, A.; Girasole, M.; Longo, G.; Mezzi, A.; Prosperi, T. *J. Mater. Chem.* **2004**, *14*, 1461−1468.

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prepared by direct irradiation ($\lambda \approx 300$ nm) of a solution of 1-undecenylic acid, but no contact angle data were given.[46]

To further investigate this, we studied the direct attachment of 1-undecenylic acid on hydrogen-terminated Si(100) by UV (254 nm) and visible (447 and 658 nm) light. The contact angles of the resulting layers prepared by visible light were 66−68° in all three cases, while in the case of the thermal reaction a contact angle of 79° was observed. The result of 66−68° in combination with ATR-IR data that display a strong C═O signal implies the presence of a significant amount of free carboxylic acid groups in the monolayer, but also suggests that no densely packed monolayer of acid-terminated alkyl chains is formed, as significantly lower contact angles are to be expected in that case (e.g., reported contact angles of acid-terminated monolayers on gold are in the range of 0 to ∼15°).[47,48] The thermally obtained value of 79° is indicative of a mixture of Si−C-bound, acid-terminated alkyl chains and Si−O-bound undecenoyl chains. The presence of the latter linkage is shown upon treatment with dilute HF solutions: short treatment of the photochemically prepared monolayers does not affect their contact angles, while the contact angle of the thermally obtained monolayers decreases to 73°, caused by the replacement of highly apolar Si−O undecenoyl chains by Si−H sites. In addition, it can be concluded that the photochemical method works as well for all three wavelengths (254, 447, and 658 nm) that were used.

Infrared Reflection−Absorption Spectroscopy. Detailed information about the structure of organic monolayers can frequently be obtained by infrared spectroscopy. Features derived from C−H stretching vibrations or functional groups such as esters or amides can reveal the presence[4−6,33,41,45,49] as well as conversion[6,33,41,45] of attached molecules. Furthermore, the precise positions of the antisymmetric and symmetric C−H stretching vibration bands in an IR spectrum of a monolayer may provide information about the quality of the monolayers, since they can be compared with those of C−H bands of isotropic and crystalline materials.[5] Due to the low absorbance of an organic monolayer and the concomitantly low signal-to-noise ratio, one usually has to rely on ATR spectroscopy, a method in which the signal-to-noise ratio is enhanced by multiple internal reflections of the IR beam in a modified double-polished ATR crystal. Alternatively, infrared spectra can also be obtained by external reflection techniques such as IRRAS.[50] IRRA spectra can be obtained using a commercially available variable-angle reflection accessory in combination with a standard IR spectrophotometer. This technique would potentially be advantageous as it allows easy measurements of vibrational features and subsequent other characterizations (X-ray reflectivity, XPS, water contact angles) all on the same sample, which is harder to do using ATR crystals (both technically and pricewise). Figure 4 gives a typical example of the C−H stretching region of an *n*-hexadecyl monolayer on hydrogen-terminated Si(100) obtained by IRRAS.

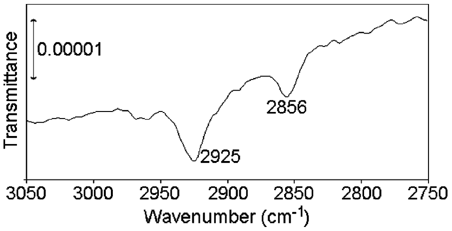

Figure 4. C−H stretching vibration region of the IRRA spectrum of a photochemically (447 nm) obtained *n*-hexadecyl monolayer on hydrogen-terminated Si(100) (IR reflection angle 68°, p-polarized light).

Table 3. IRRAS Data of the Antisymmetric and Symmetric C−H Stretching Vibrations of *n*-Hexadecyl Monolayers on Hydrogen-Terminated Si(100) and Si(111) Surfaces Obtained by Different Attachment Methods[a]

	Si(100)		Si(111)	
method	ν_a(C−H)	ν_s(C−H)	ν_a(C−H)	ν_s(C−H)
thermal	2923	2854	2923	2854
irradiation				
254 nm	2926	2856	2925	2856
371 nm	2925	2853	2925	2856
447 nm	2925	2856	2924	2855
504 nm	2924	2855	2924	2854
658 nm	2926	2855	2924	2856

[a] IRRAS data: p-polarized light, IR reflection angle 68°, in inverse centimeters. Irradiation time: 254 nm, 3 h; 371, 447, 504, and 658 nm, 15 h.

Table 4. IRRAS Data of the Antisymmetric and Symmetric C−H Stretching Vibrations of Organic Monolayers on Hydrogen-Terminated Si(100) and Si(111) Surfaces Obtained for Different 1-Alkenes and 1-Alkynes upon Irradiation with 447 nm Light for 15 h[a]

	Si(100)		Si(111)	
reactant	ν_a(C−H)	ν_s(C−H)	ν_a(C−H)	ν_s(C−H)
$CH{\equiv}CC_{10}H_{21}$	2927	2854	2925	2854
$CH{\equiv}CC_{12}H_{25}$	2925	2854	2922	2852
$CH{\equiv}CC_{14}H_{29}$	2925	2855	2922	2852
$CH_2{=}CHC_{10}H_{21}$	2926	2855	2924	2857
$CH_2{=}CHC_{12}H_{25}$	2925	2855	2925	2856
$CH_2{=}CHC_{14}H_{29}$	2925	2856	2924	2855
$CH_2{=}CHC_8H_{16}COOCH_3$ (**I**)	2930	2855	2925	2856
$CH_2{=}CHC_8H_{16}COOCH_2CF_3$ (**II**)	2931	2855	2925	2857

[a] IRRAS data: p-polarized light, IR reflection angle 68°, in inverse centimeters.

As can be seen from the spectrum in Figure 4, IRRAS clearly shows the presence of a covalently attached organic monolayer. Table 3 summarizes the IRRAS results of *n*-hexadecyl monolayers on Si(100) and Si(111). For one wavelength (447 nm, 15 h) the study was extended by the preparation of monolayers with different types of 1-alkenes/1-alkynes on Si(100) and Si(111). The results of that variation are presented in Table 4.

On average, IRRAS on the monolayers yields peak positions corresponding to antisymmetric and symmetric C−H stretching vibrations at 2925 and 2856 cm^{-1}, respectively (Tables 3 and 4). When compared with ATR data obtained on such monolayers, it is evident that these IRRAS values are all higher. The obtained values were slightly different for different types of monolayers, but—as expected on the basis of IRRAS theory[50]—also depended on IRRAS parameters, such as the incidence angle. In addition, the C−H stretching vibrations of samples that were prepared by our standard thermal procedure[51] were observed in IRRAS at consistently higher wavenumbers than in ATR (Table 3, 2923 and 2854 cm^{-1} versus 2921 and 2852

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(46) Boukherroub, R.; Wayner, D. D. M.; Wojtyk, J. U.S. Patent 6677163, Jan 13, 2004.
(47) Jennings, G. K.; Laibinis, P. E. *J. Am. Chem. Soc.* **1997**, *119*, 5208−5214.
(48) Laibinis, P. E.; Whitesides, G. M. *J. Am. Chem. Soc.* **1992**, *114*, 1990−1995.
(49) Boukherroub, R.; Wayner, D. D. M. *J. Am. Chem. Soc.* **1999**, *121*, 11513−11515.
(50) Brunner, H.; Mayer, U.; Hoffmann, H. *Appl. Spectrosc.* **1997**, *51*, 209−217.

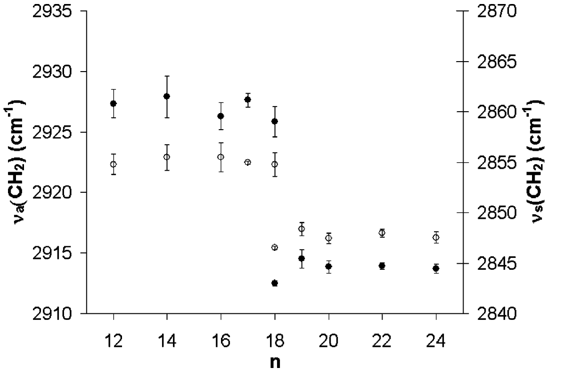

Figure 5. IRRAS band maxima for the antisymmetric (solid symbols) and symmetric (open symbols) C−H stretching vibrations of deposited alkane layers on Si(100) as a function of the chain length *n* of alkanes (C_nH_{2n+2}) (IRRAS data: p-polarized light, IR reflection angle 68°, in inverse centimeters).

cm^{-1}, respectively).[6] Therefore, a detailed investigation was desirable to obtain a clear picture of the potential of IRRAS in the study of such monolayers.

First, it was investigated whether IRRAS could also provide information about the degree of disorder (liquidlike or solidlike) in such thin layers, via measurement of thin layers of a homologous series of liquid and solid alkanes (n-$C_{12}H_{26}$ to n-$C_{24}H_{50}$) deposited on Si wafers with their native oxide layer still present. All spectra were obtained at an incidence angle of 68° with p-polarized light, since it was found for an *n*-hexadecyl monolayer on Si(100) that angles in the range of ∼60° to ∼70° gave the best signal-to-noise ratio (Supporting Information). Figure 5 shows the results for the antisymmetric and symmetric stretching vibrations for the different chain lengths.

It can be seen that the measured wavenumbers for the antisymmetric (∼2928 cm^{-1}) and symmetric (∼2856 cm^{-1}) C−H stretching vibrations of the liquid alkanes ($n < 18$) are comparable with the values found with conventional IR.[52] In contrast, the IRRAS values for the antisymmetric and symmetric C−H stretching vibration bands of the solid alkanes ($n > 17$) are found to be lower than the conventional IR values: 2914 cm^{-1} (vs 2920 cm^{-1}) and 2848 cm^{-1} (vs 2850 cm^{-1}), respectively. The results show that for the conditions used (68°, p-polarized light) application of IRRAS yields in principle a larger difference between crystalline/nonisotropic media and isotropic media than conventional infrared measurements: 14 cm^{-1} (vs 8 cm^{-1}) for the antisymmetric C−H stretching vibration and 8 cm^{-1} (vs 6 cm^{-1}) for the symmetric C−H stretching vibration. The situation is best seen at the data points obtained for n-$C_{18}H_{38}$ (mp = 29−30 °C). At temperatures <15 °C solidlike data points are obtained, while at temperatures >35 °C the peaks belonging to a liquid state are observed. In fact, during the melting of solid octadecane two sharp peaks for both the symmetric and antisymmetric C−H stretching vibrations are observed, indicating the simultaneous presence of two distinct phases, i.e., degrees of organization. As IRRAS only uses external reflections, in contrast to ATR that relies on internal reflections, IRRAS is more broadly applicable, e.g., to IR-absorbing substrates (e.g., Si_3N_x).[33] In combination with the rather straightforward and fast implementation of the measurements, and the fact that it allows multiple techniques on the same surface, IRRAS is a potentially useful and informative infrared technique.

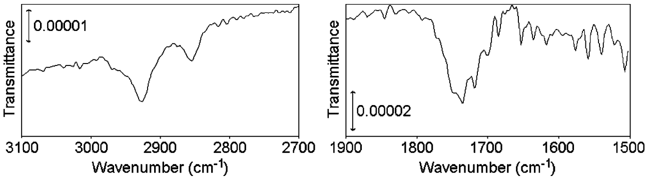

Figure 6. C−H (left) and C═O (right) stretching vibration regions of the IRRA spectrum of an n-type Si(100) modified with compound **I** using irradiation with 447 nm light (IR reflection angle 68°, p-polarized light).

Analysis of the IRRAS data in Tables 3 and 4 shows that both the thermally and photochemically prepared covalently attached monolayers on silicon seem to fall in the regime of disordered materials. This is in contrast with ATR data on the same samples, which seem to indicate a substantial degree of anisotropy, i.e., some degree of ordering, perhaps stemming from the CH_2 moieties bound most closely to the surface. A more detailed analysis of this difference would be desirable, given the ease of use of IRRAS, but is outside the scope of the present study. At the moment it suffices to say that IRRAS is a viable technique to display the presence or absence of functional groups on the surface, and that the relation between ATR-obtained values for the C−H stretching vibrations in organic monolayers on silicon and the ordering of such monolayers deserves more detailed attention.

The usefulness of IRRAS can, e.g., be shown with IRRAS measurements of monolayers of compounds **I** and **II** (two bottom entries in Table 4). Not only can the antisymmetric and symmetric C−H stretching vibrations be observed, but also a clear C═O stretching vibration indicative of an ester can be observed (Figure 6). Hydrolysis of such esters can easily be followed by IRRAS as shown by our recent work on silicon nitride.[33] All in all, we believe IRRAS measurements to be a novel and convenient tool for the study of covalently attached organic monolayers.

Effect of the Type of Silicon: Doping Type, Doping Concentration, and Orientation. Hamers and co-workers studied the photoattachment of alkenes on partly I-terminated Si(111) and Si(100),[30] and reported significant effects of the doping of the Si wafers. Following this approach, we selected four different types of Si(100) wafers, lowly and highly doped n-type and lowly and highly doped p-type Si(100), and two types of Si(111), to perform a more systematic study. The surfaces were etched and modified with 1-hexadecene using 447 nm light. The contact angles of the resulting monolayers are plotted as a function of the irradiation time (Figure 7a). For any given irradiation time, the contact angles of monolayers on n-type Si(100) are higher as compared to those of monolayers on p-type Si(100). Since the preparation conditions (including light intensity) were constant, it can be concluded that the efficiency of the photochemical monolayer formation on n-type Si(100) is higher than on p-type Si(100). From Figure 7a it can also be seen that covalent attachment follows the rate order: highly doped n ≥ lowly doped n > lowly doped p > highly doped p.

Figure 7b presents the time-dependent contact angles of 1-hexadecene-derived monolayers on lowly doped n-type and highly doped p-type Si(111). According to the contact angle data, monolayer formation on Si(111) is complete after about

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(51) Sieval, A. B.; Vleeming, V.; Zuilhof, H.; Sudhölter, E. J. R. *Langmuir* **1999**, *15*, 8288−8291.

(52) Snyder, R. G.; Strauss, H. L.; Elliger, C. A. *J. Phys. Chem.* **1982**, *86*, 5145−5150.

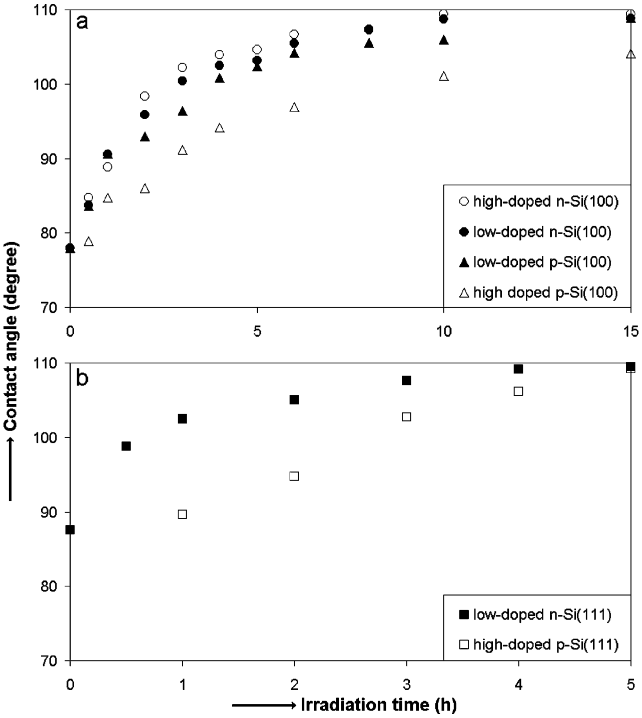

Figure 7. Water contact angles of *n*-hexadecyl monolayers as a function of irradiation time for different types of (a) Si(100) and (b) Si(111).

5 h, while it takes using the same light intensity about 10 h on Si(100). Despite the significant difference for the initially measured water contact angles for n- and p-type Si(111), the time at which the plateau value is reached depends only slightly on the doping type (4 vs 5 h for the n- and p types, respectively), and the final contact angle (~109°) is identical in both cases.

The differences between the reaction efficiency of lowly doped n-type silicon and heavily doped p-type Si(100) were also studied for 254, 371, 504, and 658 nm light (Figure 8). For all presented wavelengths, hydrogen-terminated n-type silicon surfaces are more reactive toward unsaturated hydrocarbons than p-type silicon surfaces. Note that different lamps with different intensities were used in this experiment. As a result comparison of efficiencies is only allowed for the different types of silicon that were modified with the same wavelength. The different reaction times required to obtain the plateau contact angles for the different wavelengths are in fact the result of differences in light intensity. However, it is evident that, using 254, 504, and 658 nm light, the high contact angles obtained at n-type Si(100) (~109°) could not be obtained at p-type Si(100). For practical purposes the use of n-type Si(100) or n-type Si(111) is therefore strongly advocated.

The reactivity of H-terminated silicon toward 1-alkenes in the absence of both heat and light was also studied. When a freshly etched hydrogen-terminated Si(100) sample in an argon-saturated 1-hexadecene/mesitylene solution was kept in the dark for 15 h at room temperature, the contact angle of the sample did not change (~78°). Since an increase of the contact angle would indicate monolayer formation and a decrease would imply oxidation, it can be concluded that the hydrogen-terminated surface was stable during this experiment. IRRAS showed low amounts of C−H stretching vibrations. Most likely there is some attachment due to surface defects/dangling bonds. However, to obtain a hydrophobic monolayer, light or heat is required.

While the present work clearly displays the scope of the visible light attachment, the mechanism of this reaction is much less clear. In a recent paper[31] we hypothesized that an electron/hole pair dissociation mechanism (Scheme 2, route b) would be feasible. However, two arguments cause us to refine our hypothesis. First, using scanning tunneling microscopy (STM) on partially formed monolayers of 1-decene on hydrogen-terminated Si(111), we showed, in collaboration with Eves and Lopinski, that the reaction likely proceeds via a radical chain mechanism.[53] This suggests that after some initiation process reactive sites/dangling bonds are formed at the surface that can initiate a chain reaction. Second, and more complex, is the role of supposed band bending in these materials,[30,31] since the surface is in contact with a nonconducting solution. Therefore, it is presently difficult to ascertain the degree of band bending that does actually occur in these wafers in contact with a mesitylene solution, while additionally other factors—e.g., faster oxidation of p-type hydrogen-terminated silicon than n-type hydrogen-terminated silicon—might also play a role. This complication also arises for the case of UV light initiation, as the top left graph in Figure 8 shows a dopant dependence for that wavelength as well, which cannot be fit into the mechanism (Scheme 2, route a) proposed for that reaction[9] without involving a silicon substrate-dependent parameter.

The discussion of the mechanism of the visible-light-induced reaction therefore needs to be limited to a rather broad delineation. The cleavage of a Si−H bond requires light of <350 nm, whereas <540 nm is needed for the cleavage of a Si−Si bond. Since attachment and the formation of hydrophobic monolayers can be established with visible light of wavelength even larger than 650 nm, an initiation step involving a (homolytic) cleavage of the Si−H or Si−Si bonds is not possible. Therefore, a different initiation is required. In addition, route b in Scheme 2 cannot explain the observation of island formation in the attachment of 1-decene to hydrogen-terminated Si(111) as shown by STM.[53]

We therefore tentatively propose a new mechanism in Scheme 3. Due to the formation of delocalized radical cations at the silicon surface (electrons temporarily being moved to the bulk) upon excitation thereof, this surface is susceptible to nucleophilic attack. Such a reaction may result in a Si−Si bond cleavage in a concerted manner, as in Si−Si-containing radical cations the Si−Si bond is not very strong, while the resulting Si-centered cation at the surface is highly stabilized by the neighboring Si atoms. As a result we obtain the structure at the bottom left in Scheme 3, with a β-CH radical site. This radical can pick up a H atom, and leave a Si radical at the surface that is available for the attachment of a second alkene.

A chain mechanism can also rationalize the differences in efficiency between Si(100) and Si(111). Since the Si(111) is more flat as compared to Si(100) (see, e.g., Figure 3), the chain formation on the latter surface will be hampered due to larger steps between the terraces. As a result the monolayer formation on Si(111) is more efficient.

Mixed Monolayers. An important issue in the preparation of well-defined surfaces with highly functionalized materials, e.g., for application in sensor technology, is the control over the amount and depth distribution of sensing functionalities in

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(53) Eves, B. J.; Sun, Q.-Y.; Lopinski, G. P.; Zuilhof, H. *J. Am. Chem. Soc.* **2004**, *126*, 14318−14319.

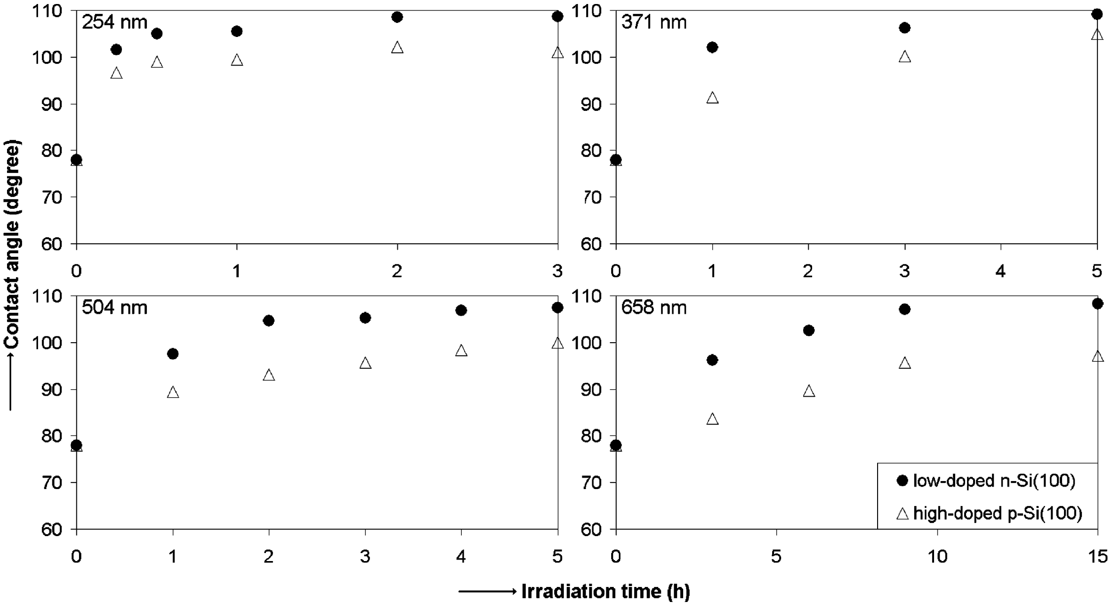
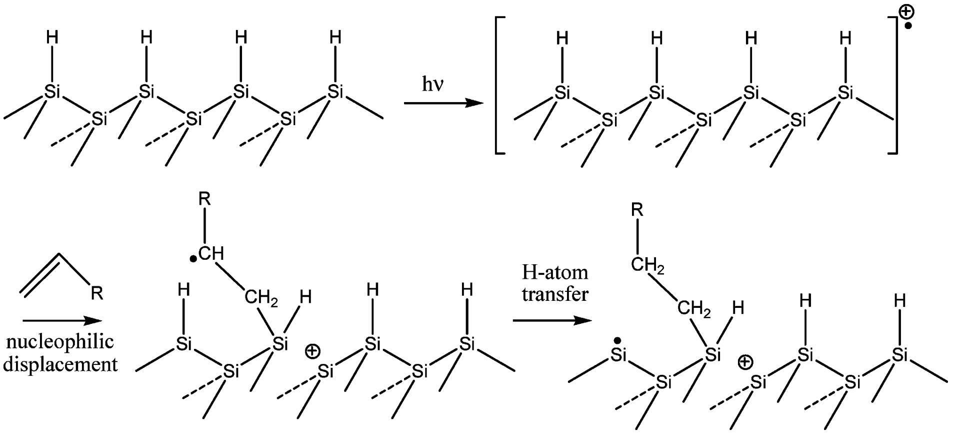


Figure 8. Contact angles of *n*-hexadecyl monolayers as a function of irradiation time for lowly doped n-type Si(100) and highly doped p-type Si(100) using 254, 371, 504, and 658 nm light, respectively.

Scheme 3. Proposed Mechanism for the Initiation of the Light-Induced Reaction



mixed monolayers. In previous work, we revealed the relation between the ratio of two esterified 1-alkenes in solution and their relative amounts in the resulting mixed monolayer as prepared with the visible light method.[31] XPS showed a linear relation between the amount of fluorine in the monolayer and the mole fraction of the fluorine-containing ester in the solution used in the preparation of the monolayer, but we could—in hindsight—not fully exclude trace amounts of carbonyl group-related photochemistry. To allow a completely unambiguous study of mixed monolayers obtained via both thermal attachment and visible light attachment, we aimed to keep the system as stable and as simple as possible by choosing 1-decene and 11-fluoro-1-undecene as a binary system. The latter compound was synthesized in two steps from the commercially available alcohol derivative. For each of the six different ratios that was used a solution of the two 1-alkenes in mesitylene was divided over the photochemical and thermal setups, to ensure the comparability of the two methods. After the modification of hydrogen-terminated Si(100), the resulting monolayers were studied with water contact angles (Figure 9) and XPS (Figure 10).

The water contact angles of the mixed monolayers were plotted against the molecular fraction of 11-fluoro-1-undecene in the mesitylene solution (Figure 9). The contact angles of monolayers prepared with 100% 1-decene (mole fraction of F-compound, 0) are the same for both preparation techniques. However, for every mole fraction >0 the contact angle of a thermally prepared monolayer is slightly higher than that of the corresponding photochemically prepared monolayer.

According to Cassie,[54] the contact angle θ of a drop of water on a heterogeneous surface made up of patches of two different types of polarities is related to the contact angle θ_i of each of the patches via the following equation:

$$\cos\theta = f_1\cos\theta_1 + f_2\cos\theta_2 \tag{1}$$

The cosine of the water contact angles of the mixed monolayers was plotted against the mole fraction (Figure 9, right). The linear trend lines have high R^2 values, indicating that Cassie's relation is applicable to this binary system. Two other binary systems on silicon[41,45] that were studied with Cassie's relation showed a lower correlation between solution composition and wetting behavior than the present data. Most likely this is related to the nature of the functional groups, which differ relatively little regarding shape, size, and polarity in the present case, and thus provides a more ideal application for the Cassie relation.

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(54) Cassie, A. B. D. *Discuss. Faraday Soc.* **1948**, *3*, 11−16.

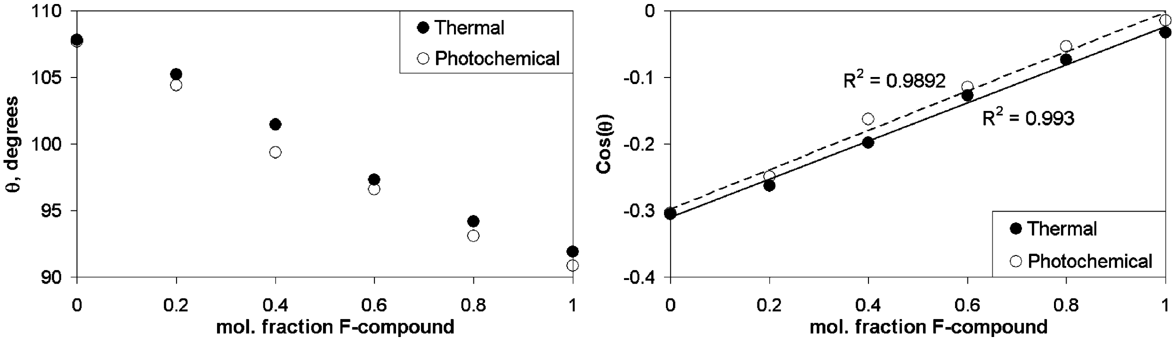

Figure 9. Water contact angle (left) and cosine of the water contact angle (right, linear least-squares fit) of mixed monolayers derived from 11-fluoro-1-undecene and 1-decene as a function of the mole fraction of 11-fluoro-1-undecene in the mesitylene solution used for the thermal (solid symbols) and visible light (open symbols) modification of H-terminated Si(100).

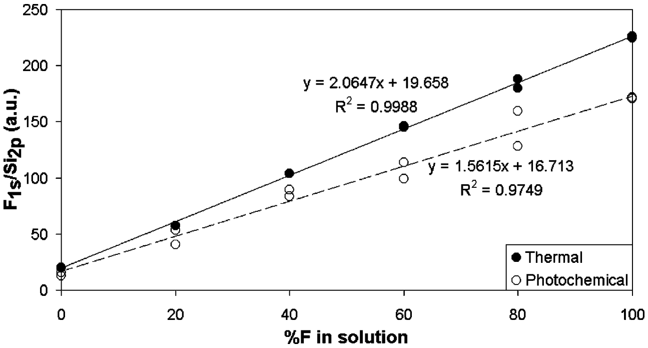

Figure 10. XPS F_{1s}/Si_{2p} ratio of mixed monolayers of 11-fluoro-1-undecene and 1-decene as a function of the percentage of 11-fluoro-1-undecene in the mesitylene solution used for the thermal (solid symbols) and visible light (open symbols) modification of H-terminated Si(100).

Figure 10 presents the results of XPS measurements (F_{1s}/Si_{2p} ratio) of the mixed monolayer, and clearly shows a linear relation between the amount of F on the surface and in solution for both the photochemical and thermal methods. The presence of a small amount of F for the 1-decene monolayer (0% 11-fluoro-1-undecene in solution) is the result of the etching procedure, as described earlier.[32] The data show that the distribution of two molecules on the surface can be controlled via their ratio in the solution that is used for the preparation. However, the slope of the given trend lines is different for the two preparation techniques, and the visible light method results according to these XPS data in a grafting density that is about 25% lower than obtained via the thermal method. It is currently unclear to which degree this is a general feature of the photochemical method, or whether this is typical for the systems in the present study, given the observation (Figure 9) that for this system the contact angles of the photochemically prepared samples are systematically somewhat lower than for the thermally prepared samples, which is not the case for other systems in the present study (e.g., Table 1). Photoreactivity of specifically the 11-fluoro-1-undecene can be excluded as its cause, not only because 11-fluoro-1-undecene does not display any significant light absorption at 447 nm, but also because gas chromatography analysis of samples before and after irradiation does not display any photoproducts, and yields a constant amount of 11-fluoro-1-undecene (in comparison to an internal standard). More detailed studies are therefore required to clarify this observation. Very recently, Liu et al. also used two techniques—IR and water contact angle measurements—to study mixed ω-carboxyalkyl/alkyl monolayers on Si(111).[45] The absorbance ratio $\nu(C{=}O)/\nu_{antisymm}(CH_2)$ showed a nearly linear relation with the mole fraction of the ester, while the correlation between surface and solution composition based on contact angles was clearly different. By stating that the Cassie relation is debatable, particularly when the surface contains two totally dispersed species, the authors believe that the spectroscopic data provide more reliable composition information than the wetting studies. Our data display a good applicability of Cassie's law, but we agree that quantitative information is better obtained from other sources, such as XPS in the present study.

Conclusions

Well-defined and highly stable organic monolayers on silicon surfaces can easily be prepared by irradiating a hydrogen-terminated silicon wafer with visible light at room temperature in the presence of a 1-alkene or 1-alkyne. Using a combination of water contact angles, X-ray reflectivity, X-ray photoelectron spectroscopy, atomic force microscopy, and infrared reflection–absorption spectroscopy, it was shown that high-quality monolayers can be formed in this manner. The reaction is rather flexible with regard to the wavelength of irradiation (371 to larger than 650 nm) and light source, and thus can avoid any light absorption by the agent that needs to be attached. These extremely mild conditions are compatible with a very large variety of biologically active moieties that can be covalently linked to the reactive alkene or alkyne functionality. This method thus allows the development of patterned, (bio)active monolayers,[32] via the combination of (bio)organic chemistry, surface science, and (nano)lithographic techniques.

Finally, a mechanism for this reaction was tentatively proposed, and the use of IRRAS for the study of organic monolayers was evaluated and proposed as an easy alternative for attenuated total reflectance IR spectroscopy.

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Supporting Information Available: Angle-dependent (0–80°) IRRAS data for a Si(111) sample modified with tetradecyne (447 nm, 15 h) and the synthesis of 10-undecenoic acid 2,2,2-trifluoroethanol ester (compound **II**) (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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