**Monolayers**

# Covalently Attached Monolayers on Hydrogen-Terminated Si(100): Extremely Mild Attachment by Visible Light**

*Qiao-Yu Sun, Louis C. P. M. de Smet,*
*Barend van Lagen, Andrew Wright, Han Zuilhof,* and*
*Ernst J. R. Sudhölter*

A "holy grail" in the attachment of monolayers on surfaces involves the use of ambient conditions that are compatible with a wide variety of functional groups. Such conditions would, for example, allow for the direct covalent attachment of many bioactive materials to a surface. In the field of covalently attached monolayers to well-defined Si surfaces presently reported attachment methods include thermal conditions and UV irradiation.[1–5] Although such reaction conditions yield stable[6,7] and densely packed monolayers,[8,9] they are too harsh to allow the use of labile bioactive materials. This situation has two ways out: In the first route, one attaches a precursor to the surface that can stand such harsh conditions, which is subsequently transformed into the bioactive monolayer. Such an approach has been taken by, for example, Hamers and co-workers,[10,11] and in the elegant DNA attachment studies of Horrocks, Houlton and co-workers.[11,13] The second route would make use of mild reaction conditions that are, in principle, compatible with such bioactive moieties. In the case of porous silicon, such an approach has been taken by Buriak and Stewart through either the use of a white-light-promoted reaction[14] or a hydride-abstracting agent.[15] Recently, Hamers reported the visible light (514 nm)-initiated modification of flat Si(111) and Si(001) surfaces by partial iodination.[16]

Herein, we further develop this second route by the formation of densely packed covalently attached monolayers by using a variety of unsaturated compounds on well-defined Si(100)–H (i.e., hydrogen-terminated) surfaces by visible light (447 nm) at room temperature. Angle-resolved X-ray photoelectron spectroscopy (ARXPS) and contact-angle measurements were used to evaluate the monolayers in detail.

Figure 1 shows the gradual formation of a hexadecyl monolayer upon irradiation of Si(100)–H wafers in the presence of 1-hexadecene. The water contact angle obtained after ≥ 10 h is 110°, which is comparable with the best literature values.[17]

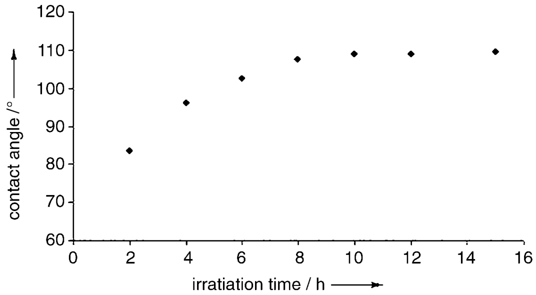

***Figure 1.*** Static water contact angle of a hexadecyl monolayer on a hydrogen-terminated Si(100) surface as function of irradiation time (447 nm).

Table 1 lists the static water contact angle of the surfaces modified by a variety of 1-alkenes, 1-alkynes, and two $\omega$-esterified-1-alkenes (compounds **I**, and **II**) by using this mild procedure, together with the corresponding results of the thermal radical reaction.[17] These results indicate that visible-light attachment yields monolayers with properties similar to those obtained from thermal radical reactions,[18] without the disadvantage of requiring a high temperature (165 °C). This has also been confirmed by using attenuated total reflection infra red (ATRIR) spectroscopy, which provided clear peaks for, for example, the antisymmetric and symmetric $CH_2$

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[*] Dr. Q.-Y. Sun, L. C. P. M. de Smet, B. van Lagen, Dr. H. Zuilhof, Prof. Dr. E. J. R. Sudhölter
Laboratory of Organic Chemistry
Wageningen University
Dreijenplein 8, 6703 HB Wageningen (The Netherlands)
Fax: (+31) 317-484-914
E-mail: han.zuilhof@wur.nl

A. Wright
Thermo VG Scientific
The Birches Industrial Estate
Imberhorne Lane, East Grinstead RH19 1UB (UK)

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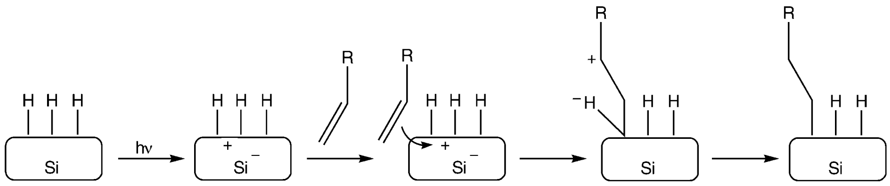
***Table 1:*** Static water contact angles of monolayers on silicon surfaces prepared by the visible-light-initiated and thermal method.[a]

| Reactants | Photochemical reaction | Thermal reaction |
|---|---|---|
| $CH{\equiv}C\text{-}C_{10}H_{21}$ | 108 | 108[b] |
| $CH{\equiv}C\text{-}C_{12}H_{25}$ | 110 | 110[b] |
| $CH{\equiv}C\text{-}C_{14}H_{29}$ | 110 | 110[b] |
| $CH_2{=}CH\text{-}C_{10}H_{21}$ | 109 | 108[b] |
| $CH_2{=}CH\text{-}C_{12}H_{25}$ | 108 | 108[b] |
| $CH_2{=}CH\text{-}C_{14}H_{29}$ | 109 | 108[c] |
| $CH_2{=}CH\text{-}C_8H_{16}COOCH_3$ (**I**) | 78 | 77[c] |
| $CH_2{=}CH\text{-}C_8H_{16}COOCH_2CF_3$ (**II**) | 85 | 88[c] |

[a] All experiments were performed at least twice; experimental error = ±1°. [b] Data taken from reference [17]. [c] Value obtained by using conditions as described in reference [17].

stretching vibrations. The precise position of the antisymmetric $CH_2$ stretching vibration ($2921.7 \pm 0.1\ cm^{-1}$ for monolayers derived from 1-hexadecene, and $2921.5 \pm 0.1\ cm^{-1}$ for those obtained photochemically from 1-hexadecyne), suggests a comparable quality as obtained for thermally prepared monolayers ($\approx 2920$–$2922\ cm^{-1}$).

Up to now, photoinduced hydrosilylation of unsaturated hydrocarbons onto H-terminated flat silicon surfaces had only been reported with UV light. The mechanism for UV-induced hydrosilylation involves photolytic homolysis of a surface Si–H bond, for example, a radical-induced reaction. Based on the Si–H bond dissociation energy on a silicon surface, a wavelength of shorter than 350[19–22]–380 nm[23] is necessary to obtain surface silicon radicals on H-terminated flat Si(111), which implies that a radical-based initiation is not in operation during the visible-light-promoted hydrosilylation reaction described here. Stewart, Buriak, and co-workers proposed an alternative mechanism to explain the white-light-promoted hydrosilylation of photoluminescent nanocrystalline silicon.[14,15] We hypothesize that this mechanism, perhaps rephrased in terms of surface plasmons,[24] depicted in Scheme 1, is also active here. If this mechanism is operative, it is expected—based on findings of Hamers and co-workers for the photo attachment of alkenes on partly iodine-terminated Si(111) and Si(001)[16]—that the required reaction time to obtain densely packed monolayers depends on the dopant concentration. This has indeed been found: after 5 h Si(100)–H with low dopant concentration (p- or n-type) yields contact angles ≈100°. However, heavily doped p-type Si(100)–H is much harder to modify, and yields after 5 h a contact angle of ≈90°, and after 10 h of only 104°, in line with the effects of the dopant on the band bending.



***Scheme 1.*** Proposed mechanism for the hydrosylilation of Si(100)–H with 447 nm light.

Fluorine-containing alkenyl esters were synthesized and photoattached to Si(100)–H wafers. Thus obtained monolayers of $CH_2{=}CHC_{13}H_{26}CO_2CH_2CF_3$ (**III**)[25] were analyzed by X-ray photoelectron spectroscopy (XPS), a very useful tool for the study of covalently attached monolayers on silicon.[10,11,16,19,22,26–34] Figure 2 shows the $C_{1s}$, $F_{1s}$, and $Si_{2p}$ regions of the resulting XPS spectrum. The $C_{1s}$ region spectrum shows peaks from 288 to 294 eV, which can be assigned to the different carbons in the trifluoroethyl ester moiety.[10] The presence of $C_{1s}D$ (294 eV) and $F_{1s}$ (689 eV) signals indicates that a trifluoroethyl ester-terminated monolayer was formed on the Si(100)–H surface. Additionally, the silicon spectrum shows very little oxidation of the surface as evidenced by the small signal in the 101–103 eV region. The results are comparable to those obtained with UV light (254 nm) to attach the trifluoroethyl ester of undecylenic acid onto the Si(111)–H surface.[10]

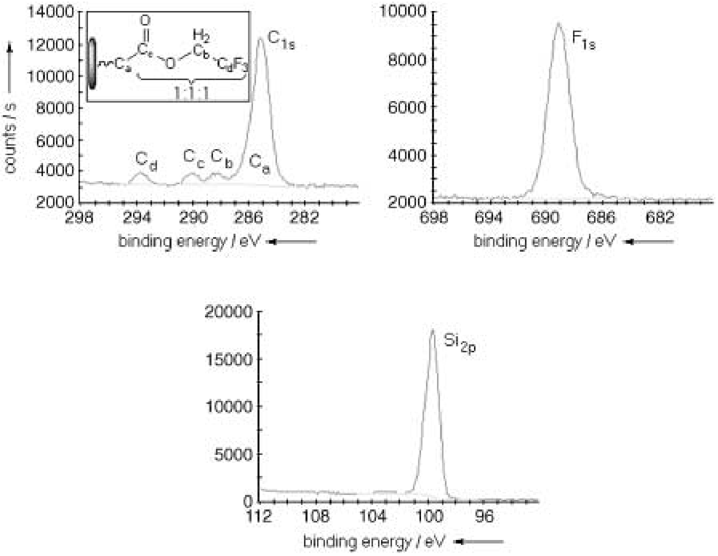


***Figure 2.*** X-ray photoelectron region spectra of a monolayer of compound **III** on Si(100)–H prepared by the method of visible-light-induced hydrosilylation.

An important issue in the preparation of surfaces for the application in sensor technology is the control over the amount and depth distribution of sensing functionalities in mixed monolayers. To study the relation between the ratio of two 1-alkenes in the solution and their relative amounts in the resulting mixed monolayer, mixed monolayers of compounds **I** and **II** were prepared. Figure 3 shows that the amount of F atoms (as measured by XPS) of the mixed monolayers increases linearly with an increasing molar fraction of compound **II** in the alkene solution from which the samples were prepared. This result implies that one can obtain a surface that can easily be defined by solution properties. Such a relation has previously been proposed based on indirect fluorescence labeling.[35]

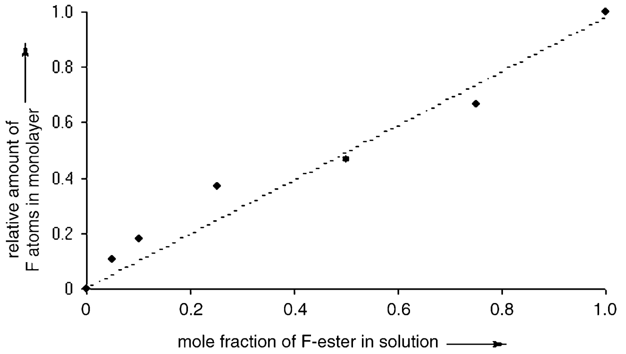


*Figure 3.* Linear correlation of the amount of F atoms in the photochemically prepared monolayers as function of the mole fraction of trifluoroethyl ester **II** in mixed solutions.

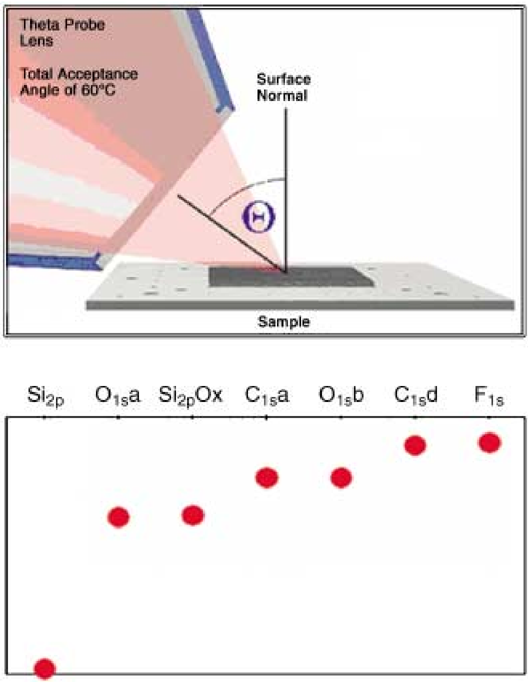


*Figure 4.* Schematic representation of the two-dimensional detection system (top), and relative depth profile of the elements of a Si sample modified by compound **III** (bottom).

Since the diameter of the probe molecule—rhodamine—is larger than that of an alkyl spacer, it is unlikely that the observed linearity from a 0% to a 100% rhodamine-substituted monolayer can be attributed to a linearly changing composition of constant monolayer thickness/packing density of a densely packed monolayer. In addition, ATRIR has been used to study to the ratio of the ester carbonyl stretch to the total methylene asymmetric stretch as a function of the mole fraction of ethyl undec-1-enylate in 1-decene.[36] Although qualitatively in line with the present finding, quantification of monolayer IR data is harder than that of XPS data. The value of XPS was, for example, shown by detailed analysis of mixed monolayers of **III** with 1-hexadecene. The fluorine probe works well since quantitative XPS allows one to obtain the amount of F atoms of the surface directly for the total concentration range, while the constant packing density of the monolayer of both thermally and photochemically prepared monolayers could be ascertained from the $C_{1s}$A signal.

Apart from with conventional XPS, the monolayers were also studied with parallel angle-resolved XPS (ARXPS) by using a 2D microchannel detector (MCD) that measures the intensity of the photoelectron emission as a function of emission angle. As a result the angle-resolved data are acquired simultaneously (Figure 4, top). This MCD permits ARXPS experiments without tilting the sample, and with a concomitantly constant analysis area for all detection angles. As a result, unparalleled resolution can be obtained with respect to the distribution of depths of the elements on the surface. Figure 4 (bottom) depicts a relative depth profile of such a mixed monolayer of compound **III**, for a monolayer of only 1.4 nm total thickness. To the best of our knowledge, this is the first report of an ARXPS-based relative depth profile on an ultrathin organic monolayer. The relative depth profile locates bulk Si at the bottom ($Si_{2p}$), subsequently the Si peak of Si atoms bound to O ($Si_{2p}$Ox), and the corresponding O atoms ($O_{1s}$A). Then the carbon-atom signals of the alkyl spacer and the oxygen-atom signals of the ester are found ($C_{1s}$A and $O_{1s}$B), while on top the signals are found for $C_{1s}$D and $F_{1s}$ that belong to the $CF_3$ group (data for intermediate $C_{1s}$B and $C_{1s}$C are not shown). Signals for $F_{1s}$ appear lower than $C_{1s}$D owing to trace amounts of unresolved F atoms bound to the Si surface, which result from the etching step.

We reported for the first time a visible-light induced reaction for attaching functional monolayers onto the Si(100)−H surface. According to the water contact angle the quality of monolayers derived in this way is as good as that of monolayers obtained by the thermal reaction. High-resolution ARXPS was used to provide detailed information about the depth distribution of the elements in the monolayer. Furthermore, it was shown by quantitative XPS that for appropriately sized functional groups, the surface composition can be easily defined by the solution composition. The combination of these techniques opens an attractive avenue for the attachment and characterization of (bio)active functionalization of monolayers on silicon,[37] including a variety of lithographic techniques.

## Experimental Section

Materials: Single-polished Si(100): n-type, 500–550 μm thick, resistivity 1–2 Ωcm (Seltec Silicon, Mitsubishi Silicon America), p-type, 375 μm thick, resistivity 1–2 Ωcm (Bayer Solar Freiberg, Germany), p-type, 475 μm thick, resistivity 0.015–0.025 Ωcm (Okmetic Inc., USA). Other chemicals and purifications as in references.[7,17]

XPS and ARXPS measurements: XPS and ARXPS analyses were performed on a Theta Probe (Thermo VG Scientific, UK) by using a monochromatic $Al_{K\alpha}$ X-ray source with a 400 μm spot runs at 100 W under UHV conditions. The higher-resolution XPS data in Figure 2 were acquired in standard (non angle-resolving) mode by using scanned spectra at a pass energy of 100 eV. The snapshot mode of acquisition was used for the ARXPS data. This acquires spectral data across the full detector width at a fixed analyzer energy. The ARXPS snapshot spectra were acquired from 500 × 1 s frames at a pass energy of 150 eV. Sixteen angles were measured in the range of 23–83°. The relative surface sensitivity for a particular chemical species was determined by calculating the ratio of the sum of the relevant peak areas at three bulk-sensitive angles (23–35°) and the sum of the equivalent peak areas at three surface-sensitive angles (65–75°).

Monolayer preparation: Si(100) samples were cleaned in piranha solution ($H_2SO_4$:$H_2O_2 = 2:1$) at 90 °C for 2 h, and subsequently etched by using 2.5 % HF for 2 min. The alkene solution was flushed with $N_2$ for 30 min before and for 30 min after putting the fresh Si(100)–H wafer into the solution, before the light was turned on. The visible-light-initiated reaction was performed by irradiation of a wafer-containing 0.1M solution of 1-alkene/1-alkyne in mesitylene with monochromatic 447 nm light (phosphor-coated pen lamp from Jelight Company, model 84-247-2, 32 nm bandwidth, $\approx 3\,\mathrm{mW\,cm^{-2}}$ intensity at 2 cm) from 0.5 cm for 15 h under a $N_2$ atmosphere. Afterwards, the surface was excessively rinsed with PE40/60, EtOH and $CH_2Cl_2$.

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