

Photoactivated Preparation and Patterning of Self-Assembled Monolayers with 1-Alkenes and Aldehydes on Silicon Hydride Surfaces

Franz Effenberger,* Günther Götz, Bernd Bidlingmaier, and Markus Wezstein

The preparation, investigation, and patterning of self-assembled monolayers (SAMs) for the chemical modification of surfaces is currently an intensively researched area worldwide.^[1, 2] We have already reported on the structure and properties of mono- and multilayers derived from terminally functionalized organosilanes on hydroxylated silicon surfaces.^[3] We are interested, however, in special applications of the coated silicon surfaces. In these cases the SiO₂ layers of hydroxylated silicon surfaces, which are always present, would be disturbing.^[2, 4] We have therefore investigated the formation of SAMs on silicon in such a way as to avoid the presence of an oxide layer.

Chidsey et al.^[5] have recently reported the preparation of stable SAMs of organic compounds on silicon, in which the organic layer is directly bound to silicon—without a SiO₂ interlayer. These SAMs were obtained by diacyl peroxide catalyzed reactions of 1-alkenes on hydrogen-terminated Si(111) surfaces.^[5] The disadvantages of this method are the unfavorable inclusion of acyloxy radicals in the monolayer, which are detrimental to the quality of the layer,^[1b] and the relatively low coverage.^[5] If these reactions are carried out under thermal conditions instead of using peroxide catalysts, liquid-like layers are obtained rather than solids.^[5b]

In connection with our investigations into the fundamentals of molecular electronics the incorporation of unsaturated compounds (such as polyenes and oligothiophenes) in SAMs is also of interest.^[6] We have therefore investigated alternatives to the diacyl peroxide catalyzed reactions of alkenes with silicon hydride surfaces for the formation of SAMs. The reaction of hydrogen-terminated Si(111) surfaces with 1-alkenes can also be achieved by irradiation with light. Table 1 shows a comparison of the formation of SAMs on Si(111)-H surfaces with 1-octadecene **1**, initiated by both diacyl peroxide (according to the literature procedure^[5]) and irradiation with a 150-W mercury vapor lamp.

The SiH surface was prepared by treatment of oxidized Si(111) wafers with an ammonium fluoride solution.^[7] The coverage was determined analogous to published methods^[3c] by quantitative evaluation of the IR bands of the symmetric and asymmetric methylene vibrations, $\nu_{as}(\text{CH}_2)$ and $\nu_s(\text{CH}_2)$. Table 1 shows that with respect to the coverage, photoactivation gave results comparable with those from peroxide activation without the disadvantages associated with the latter.

[*] Prof. Dr. F. Effenberger, Dr. G. Götz, Dipl.-Chem. B. Bidlingmaier, Dipl.-Chem. M. Wezstein
Institut für Organische Chemie der Universität
Pfaffenwaldring 55, D-70569 Stuttgart (Germany)
Fax: (+49) 711-685-4269
E-mail: franz.effenberger@po.uni-stuttgart.de

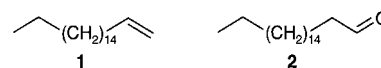


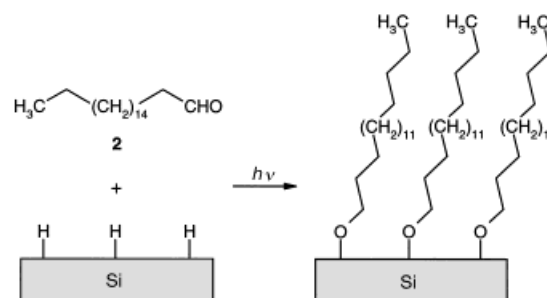
Table 1. Comparison of SAMs with octadecene **1** and octadecanal **2** on Si(111)-H surfaces.^[a]

Reactants (neat)	<i>t</i> [h]	<i>T</i> [°C]	$\nu_{as}(\text{CH}_2)$ [cm ⁻¹]	Coverage [%] ^[b]	Contact angle θ_a (H ₂ O) [°]
[C ₁₇ H ₃₅ C(O)O] ₂	1.5	100	2918.7	50	91
[C ₁₇ H ₃₅ C(O)O] ₂ : 1 (1:1)	1.0	102	2918.6	57	96
[C ₁₇ H ₃₅ C(O)O] ₂ : 1 (1:9)	1.5	101	2920.0	48	91
1	24	20–50 ^[c]	2920.5	55	95
1 ^[d]	20	20–50 ^[c]	2922.4	21	–
2	21	20–50 ^[c]	2916.8	97	105
OTS ^[e]	15	20	2917.7	100	106

[a] Initiation of layer formation by dioctadecanoyl peroxide [C₁₇H₃₅C(O)O]₂ catalysis^[5b] or by irradiation with a 150 W mercury vapor lamp. [b] Based on octadecyltrichlorosilane(OTS) films on hydroxylated Si(100) surfaces with 100% coverage. [c] Temperature increase to 50 °C during the irradiation. [d] In solution, 1:hexadecane = 9:1. [e] In solution.^[3c]

Since in the reaction of the 1-alkenes activation with H₂[PtCl₆] did not give better results,^[8] we investigated other compounds for the preparation of SAMs on Si(111)-H surfaces. Giese et al.^[9] reported that hydrosilylation of alkenes and carbonyl compounds with tris(trimethylsilyl)silane can be catalyzed not only by free-radical initiators but also by photoactivation. Based on these results we studied the mode of reaction of aldehydes with SiH surfaces. Under the conditions for the reactions with 1-octadecene (see Table 1), we obtained well-ordered monolayers with surprisingly high coverage (97% based on OTS with 100%) by the photoactivated reaction of octadecanal **2** with hydrogen-terminated Si(111) surfaces.

Scheme 1 illustrates the formation of a monolayer with the long-chain aldehyde **2** on a SiH surface. The linkage of **2** to the SiH surface was detected by X-ray photoelectron spectro-



Scheme 1. Schematic illustration of layer formation with octadecanal **2** on a SiH surface.

scopy (XPS):^[10] the signals in the spectrum at 286.3 BeV (C 1s C–O), 100.9 and 101.6 BeV (Si–O 2p_{3/2} and Si–O 2p_{1/2}, respectively) indicate covalent bonding.

In order to obtain detailed information about the scope of the application of the new method to the preparation of SAMs on silicon surfaces we investigated the dependence of the layer formation on the wavelength of the irradiating light (Figure 1) and on the reaction time (Table 2). The optimum

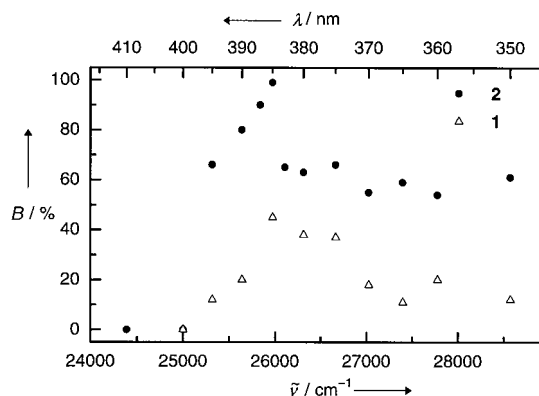


Figure 1. SAM formation with neat octadecene **1** and octadecanal **2** on a SiH surface as a function of the wavelength of the incident light. The coverages are not corrected for either the lamp spectrum or the spectral transmission of the spectrometer. B = Coverage.

Table 2. SAM formation with neat octadecanal **2** on a Si(111)-H surface as a function of the irradiation time with polychromatic light.

t [min]	$\nu_{\text{as}}(\text{CH}_2)$ [cm ⁻¹]	Area $\nu_{\text{s}}, \nu_{\text{as}}(\text{CH}_2)$	Coverage [%] ^[a]
1	2922	0.0357	39
3	2918	0.0746	82
5	2917	0.0943	103
30	2916	0.0975	106
60	2916	0.0978	107
120	2916	0.0833	91

[a] Based on OTS films with 100% coverage.

wavelength for layer formation occurs at about 385 nm. On the basis of the dissociation energy of Si–H bonds^[11] (81 kcal mol⁻¹ for tris(trimethylsilyl)silane, corresponding to 354 nm^[11a]) the energy at longer wavelengths, as expected, is indeed not sufficient to initiate the reaction (Figure 1). However, that irradiation at shorter wavelengths would lead to lower coverage was not expected. From the intensity distribution of the XBO lamp, the effectiveness of the monochromator, and the transmission behavior of the irradiation cuvette result that the relative intensity of the irradiation decreased continuously from 400 to 350 nm; the optimum layer formation at 385 nm does not depend, then, on the intensity of the irradiation. Since in the reactions of **1** optimum layer formation also occurs at 385 nm (Figure 1), photoactivation of the carbonyl or the C–C double bond can be ruled out as an explanation for the wavelength optimum for these reactions. The results of FT-IR measurements with regard to the time dependence (see Table 2; coverage, $\nu_{\text{s}}(\text{CH}_2)$ and $\nu_{\text{as}}(\text{CH}_2)$) reveal a well-ordered monolayer with a high coverage already after 5 minutes.

In all preparations of SAMs^[1–3] until now a direct lateral patterning of SAMs was not possible owing to initial chemically uniform surfaces (e.g. gold, hydroxylated or hydrogenated silicon) and the also homogeneous subsequent reaction with the self-assembling compounds. However, the light-induced preparation of SAMs described here allows, with the use of suitable masks, direct patterning of surfaces by applying the self-assembly technique. From the various materials with potential masking properties, the films used

in the manufacture of printed circuits proved to be particularly advantageous.^[10] In the reaction with **2** we could demonstrate, by means of IR spectra, that covering part of the Si(111)-H surface resulted in the formation of a SAM layer only on the light exposed part of the Si(111)-H surface. In addition we were able to show that the nonirradiated part of the SiH surface remained completely reactive.

Since the results of these experiments indicated that basically, a lateral patterning of SAMs is possible by photoactivation, we used a structured mask and carried out a light-induced coating of a SiH surface with **2**. The differing wettabilities of the coated and noncoated areas of the silicon allowed the patterned silicon surface to be observed directly under a microscope (Figure 2).^[10]

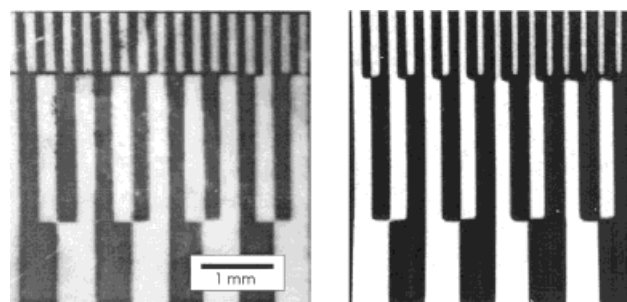


Figure 2. Microscopy images of a patterned SAM with octadecanal **2** (left) and the corresponding mask (right).

In the penultimate paragraph of a recently published review by Whitesides et al.^[2] the following comment was made on the future of “soft lithography”: “In particular, systems that form SAMs directly on semiconductors and are optimized for compatibility with current processes (especially etching with reactive ions) and materials are required”. The results presented here on the light-induced, direct lateral patterning of SAMs on SiH surfaces are certainly an interesting and important contribution to the attainment of this aim.

Experimental Section

FT-IR spectra were measured with a Bruker-IFS-66V spectrometer. All reactions were carried out in an inert gas atmosphere. Silicon wafers (Si(111), p-type, Siltronix) were used. Irradiation was carried out with an HBO-mercury vapor lamp (150 W).

Monolayer formation: The SiH substrate, prepared by etching with fluoride ions,^[7] was immersed in a melt of **1** or **2** in a glass cuvette and irradiated for 20–24 h. After removal from the cuvette the substrate was washed several times with CH₂Cl₂ and wiped with cotton.

Monolayer formation with **1 and **2** at different wavelengths:**^[10] Layer formation (see above) was carried out at 60 °C by irradiation with an XBO lamp (450 W) fitted with a double monochromator (Jarrell Ash Co., 82–440) with a half-band width of 1.3 nm. The coated substrate was cleaned as described above.

Time-dependent monolayer formation with **2:** As described above, the SiH substrate^[7] was irradiated in a melt of **2** for the times given in Table 2 and subsequently cleaned.

Preparation of the masks: The structures were drawn with the program Freehand 5.0 and printed directly with a laser photosetting system (Linotronic 530, Linotype-Hell, resolution 2540 dpi) on polymer films (Fuji Laser recorder film F 100).

Lateral patterning: The SiH substrate was covered with a mask, the aldehyde was added, and melted. For monolayer formation and cleaning see above.

Visualization of structures: The substrate with the monolayer was wetted under a microscope (Carl Zeiss, 20-fold enlargement) with a few drops of a mixture of 2-propanol and universal oil (Lubricant Consult GmbH). The pattern formed after a few seconds was photographed.

XPS measurements: XPS measurements were made with a Leybold MAX-200 spectrometer with $\text{MgK}\alpha$ radiation (300 W) under a pressure of 10^{-9} mbar. The superimposed signals were separated and assigned by calculations with the manufacturer's software (DS 100). The signals observed were O 1s (532.1 BeV), C 1s C–C (284.6 BeV), C 1s C–O (286.3 BeV), Si–O $2p_{3/2}$ (100.9 BeV), Si–O $2p_{1/2}$ (101.6 BeV).

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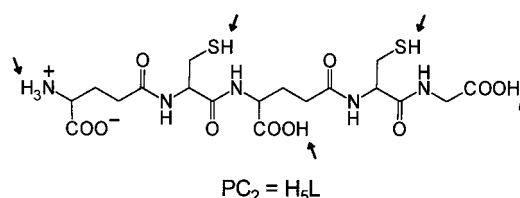
A Coordination-Chemical Basis for the Biological Function of the Phytochelatins**

Jens Johanning and Henry Strasdeit*

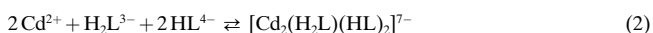
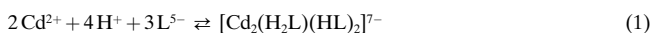
*Dedicated to Professor Bernt Krebs
on the occasion of his 60th birthday*

Organisms respond to heavy-metal stress, caused by toxic metals, with different detoxification strategies.^[1] Thus plants synthesize short peptides of the composition $(\gamma\text{-Glu-Cys})_n\text{-Gly}$ ($n = 2–11$), the phytochelatins (PC_n),^[2] which coordinate to metal ions and thereby decrease the toxicity of these ions.^[3] The best characterized phytochelatin complexes are those of cadmium.^[4] However, the bioinorganic chemist also has only a rough picture even in this case because of the heterogenic character of the native complexes. Furthermore there is a lack of data on the thermodynamic stabilities, which are essential for a better understanding of the biological function.

We have therefore examined the system $\text{Cd}^{\text{II}}/\text{PC}_2$ by potentiometric titration^[5] under exactly defined conditions (see Experimental Section) to gain information about the complexes occurring there. PC_2 , the simplest phytochelatin, is a pentabasic acid (H_5L). Starting from the fully protonated



form HPC_2^+ ($= \text{H}_6\text{L}^+$), the protonation constants $\text{p}K_1 = 2.39(5)$, $\text{p}K_2 = 3.18(3)$, $\text{p}K_3 = 4.01(7)$, $\text{p}K_4 = 8.75(9)$, $\text{p}K_5 = 9.03(3)$, and $\text{p}K_6 = 10.04(12)$ were obtained for the free ligand.^[6] The complex species that were detected are listed in Table 1. The $\lg\beta$ values given therein include the protonation equilibria of the ligands [Eq. (1)]. They are those quantities that have been directly determined in the refinements. In coordination-chemical considerations, however, $\lg K$ values calculated from them are more useful. They allow equilibria such as that given in Equation (2) to be described quantitatively.



The species models were developed and assessed on the basis of general criteria.^[5] In addition some special guidelines were available:

[*] Priv.-Doz. Dr. H. Strasdeit, Dipl.-Chem. J. Johanning
Fachbereich Chemie der Universität
Carl-von-Ossietzky-Strasse 9–11, D-26129 Oldenburg (Germany)
Fax: (+49) 441-798-3329
E-mail: strasdeit@chemie.uni-oldenburg.de

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