*ADVANCED MATERIALS*

High-Quality Alkyl Monolayers on Silicon Surfaces**

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Covalent attachment of functionalized monolayers onto silicon surfaces (see Figure for examples) is presented here as a strategy for surface modification. The preparation and structure of both unfunctionalized and functionalized alkyl-based monolayers are described, as are potential applications, for example, in the surface passivation of Si solar cells and for photopatterning of silicon surfaces.
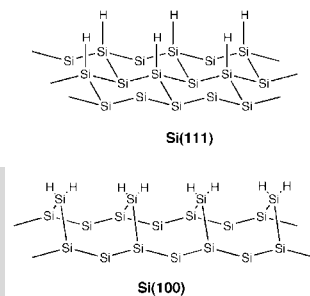
1. Introduction

Controlled modification of surface properties is a key feature in the development of chemically based nanotechnology. An interesting approach involves the deposition of a monolayer of material on a surface. The most well-known example is formed by thiol monolayers on gold surfaces. More recently, an additional class of surface modifications has become available via the covalent attachment of functionalized monolayers on silicon surfaces. Since the properties of these monolayers differ in several important aspects from the thiol-on-gold systems, this class of functionalized surfaces has great potential.

First, the procedure to make functionalized monolayers on silicon is easy. By simple "bench chemistry" under atmospheric pressure hydrogen-terminated silicon surfaces (both Si(100)–H and Si(111)–H) react with alkenes and alkynes by heating, resulting in the formation of a monolayer.[1] Schematically this process is depicted in Figure 1. At the start, the Si surface has to be cleaned (removal of silicon oxide) by treatment in HF, and subsequently reaction of the hydrogen-terminated Si surface with the alkene or alkyne can take place. Second, the monolayer is attached to the surface via a very stable covalent Si–C bond,[2] which results in a durable monolayer 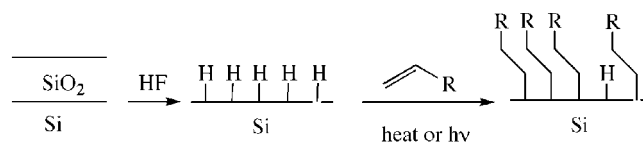under a variety of conditions, including boiling organic solvents or water, hot acid or base, or the presence of fluoride anion. The monolayer is also thermally highly stable, as was shown by measurements under ultrahigh vacuum conditions up to 615 K.[3] These features prompted a detailed physical investigation of the mechanism of formation and of the resulting surface properties.

Fig. 1. Synthesis of covalently attached alkyl monolayers on silicon surfaces.

2. Formation

The preparation of the monolayer starts with cleaning of the Si surface from oxides. The appropriate method depends on the nature of the Si surface, and differs slightly for Si(100) and Si(111) surfaces. At the start a Si wafer is etched (Si(100): 2 min by 2 % HF; Si(111): 5 min in 40 % NH$_4$F). This yields the hydrogen-terminated Si(100) and Si(111) surfaces depicted in Figure 2. For the Si(100)–H interface the surface silicon atom is bound to two sub-surface silicon atoms and to two surface hydrogen atoms (=SiH$_2$). At the Si(111)–H surface the surface silicon atoms are bound to three sub-surface silicon atoms, while the fourth bond is directed to the surface hydrogen atom ($\equiv$Si–H). It has been proposed that during thermal activation a silicon–hydrogen bond is homolytically cleaved, resulting in a silicon-centered radical, a so-called dangling bond (=SiH$^\bullet$ and $\equiv$Si$^\bullet$, on the Si(100) and Si(111) surfaces, respectively).[1] The alkene or alkyne subsequently adds to the Si radical in an anti-Markovnikov fashion, and forms a covalent bond between the silicon atom and the terminal alkene or alkyne carbon atom, in which the radical cen-

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ter becomes positioned at the β-carbon atom. This highly reactive radical would then finally abstract a hydrogen atom from a neighboring surface silicon atom, forming a Si radical again, which causes the chain reaction to propagate by reaction of this radical with another alkene or alkyne molecule. This mechanism is similar to the well-known hydrosilylation of terminal alkenes,[4] and explains the observed close packing of the alkyl chains in the monolayer. Very recently, however, some doubt has been cast on this mechanism based on IR studies on deuterium-substituted surfaces.[5] The interpretation of those IR data is incompatible with the initial proposal by Chidsey and co-workers, and incompatible with our observation that in dilute alkene solutions more bulky solvents yield better monolayers than solvents consisting of small or linear molecules.[6] As a result the mechanism of monolayer formation clearly deserves more detailed investigations.

The initial thermal procedure to prepare the monolayers required the use of neat alkenes or alkynes.[1] Such high alkene or alkyne concentrations are advantageous for the formation of well-ordered monolayers, as they would speed up the propagation steps in a chain reaction leading to monolayer formation (vide supra). However, in this procedure large amounts of material are needed and only a small fraction of the alkene or alkyne ends up in the monolayer. We have therefore systematically investigated the possibility of using dilute solutions of alkenes as alkene source.[6] The aim of that study was to find out which conditions should be used to obtain a dense, well-ordered monolayer with a minimum amount of alkene. To this aim a range of solute concentrations and solvents was used, and the quality of the resulting monolayer was studied by water contact angles. The best compromise between small amounts of alkene and high-quality monolayers was obtained by using refluxing mesitylene for 2 h (b.p. = 166 °C). In this solvent the use of relatively low concentrations of 1-hexadecene (2.5 vol.-%) still results in dense, well-ordered monolayers, as shown by water contact angles of 109° and 98° (advancing and receding angles, respectively). In other investigated solvents higher alkene concentrations were needed to obtain a high-quality monolayer. Generally a solvent appears to be more suitable when the shape of the solvent molecule is more unlike that of the alkyl layer, and "bulky" aromatic solvents (mesitylene, *m*-xylene) were better than toluene and much better than high-boiling alkanes.[6] This procedure is an important improvement, because in this way the required amount of alkene or alkyne is reduced by a factor of 20–40 in an expedient manner without loss of layer quality.

Several other methods to prepare covalently attached monolayers on crystalline Si surfaces have been reported, including the reaction of chlorinated silicon with Grignard reagents and Lewis acid–mediated hydrosilylations.[7,8] As these require different starting materials than 1-alkenes or 1-alkynes, they represent different routes to covalently attached monolayers. Since the ease of formation of a specific mono-
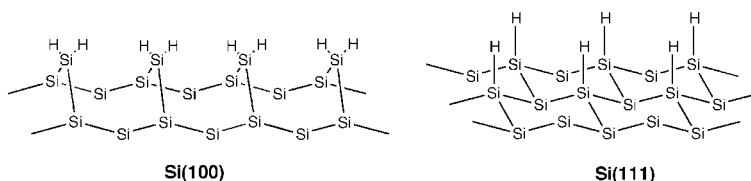

Fig. 2. Schematic representation of hydrogen-terminated Si(100) and Si(111) surfaces.

layer is usually related to the availability of the starting material, the different methods complement each other. It should in this context be said that it is hard to produce really clean, dense monolayers by Lewis acid catalysis and Grignard chemistry. The use of Grignard chemistry will usually lead to undesirable contamination of the surface by metal ions.[7] The disadvantage of Lewis acid catalysis is caused by a smaller percentage of coverage of the surface, which diminishes the long-term stability of thus produced monolayers in comparison to layers prepared by the photochemical, direct thermal, or Grignard methods.[8] The direct thermal method using dilute solutions developed in our laboratory does not have these drawbacks.[6,9]

3. Monolayer Structure

From X-ray reflectivity and IR measurements on unfunctionalized alkyl monolayers, it was inferred that the alkyl chains form a densely packed, well-ordered monolayer.[1,9] In fact, the frequency of the asymmetric methylene C–H stretch vibration in these layers indicates an order that resembles that of crystalline alkanes. In these monolayers, the alkyl chains are tilted by ca. 30° from the surface normal.[9] Unfunctionalized alkyl monolayers are highly hydrophobic, as was concluded from respective advancing and receding water contact angles of 113° and 105° on Si(111)[1] and 109° and 98° on Si(100).[6] In line with the measured layer thickness and order, this suggests that the outer face of the monolayer consists of terminal methyl groups. This was confirmed by molecular modeling studies (vide infra), which yielded a minimum energy structure of such layers as depicted in Figure 3.[10] The thus formed monolayer provides excellent protection of the silicon substrate against oxidation. This is most clearly shown by X-ray photoelectron spectroscopy (XPS) measurements (Fig. 4), which do not show any oxide formation even after
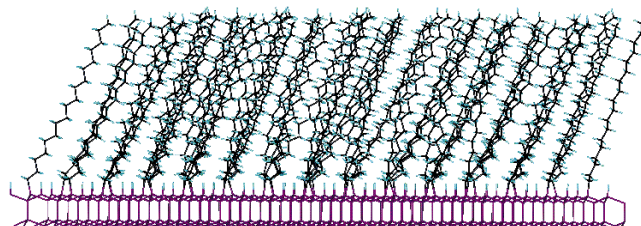

Fig. 3. Optimized structure of octadecyl monolayer on Si(100) surface (obtained from PCFF molecular mechanics calculations; see text). Picture reproduced with courtesy of the American Chemical Society from [10].
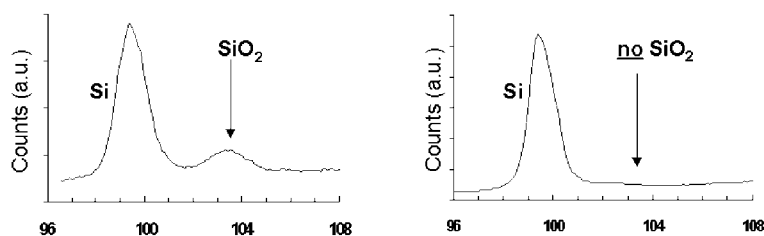
Fig. 4. XPS measurements (in eV) of an untreated Si wafer (left) show formation of SiO₂, while attachment of the covalent monolayer (right) prevents oxidation even after months!

storage of the monolayer under atmospheric conditions at room temperature for 4 months.[9] Since oxidation involves the presence of water at the surface, it may be concluded that the dense hydrophobic layer prevents the penetration of water through the monolayer. As complete coverage does not mean complete replacement of Si–H by Si–C bonds (vide infra), at maximum replacement around 61 % of the $\equiv SiH_2$ sites on the hydrogen-terminated Si(100) surface are substituted by an alkyl group, while ca. 53 % of the Si atoms on Si(111) can be substituted. This is related to the unit cell sizes of Si(100) [14.75 Å²] and Si(111) [12.77 Å²] compared to the diameter of an all-*trans* alkyl chain [18.6 Å²]. From our XPS results (Fig. 4) and those of Chidsey[1] and Wayner[8] it can be concluded that these remaining silicon hydrides are only transformed to silanol groups by the action of oxygen.

An interesting issue is the percentage of surface coverage by alkyl chains. The experimentally reported values[1,9] are close to the theoretical maxima, which implies the formation of truly dense layers. This degree of coverage was confirmed by molecular modeling studies on monolayers derived from 1-octadecene.[10] Using the advanced polymer consistent force field (PCFF) the steric energy per alkyl chain in the monolayer can be computed for different degrees of coverage and for different surface substitution patterns at a fixed percentage of coverage. As a monolayer is present over areas that are much larger than molecular dimensions (as was, for example, shown by contact-mode atomic force microscopy (AFM) data[8]), proper modeling of monolayer surfaces requires the use of extended surfaces. In principle this can be done in two ways: a) via modeling of a large surface area, or b) via modeling of a relatively small surface area that is treated with periodic boundary conditions, i.e., the surface is periodically repeated in two dimensions. The first approach requires the use of very large surface areas, as the outer sides of any finite surface display edge effects. These are caused by the fact that for any given alkyl chain the number of neighboring alkyl chains at the edge of a surface deviates from that in the inner part of a surface. From our own results it became apparent that modeling of densely covered hydrogen-terminated Si(111) surfaces requires as many as 150 alkyl chains (and thus around 300 $\equiv$Si–H groups at the surface) to get convergence on the properties of the alkyl chains in the middle of the surface.[11] With a smaller modeled surface, the properties of the surface are largely determined by the edges, and representation of the experimentally observed well-ordering of monolayers is not possible.

A much better approach therefore is the second one, which in addition is computationally much less demanding. In this approach a two-dimensionally repeating box of limited size is used to model the surface. If the box size is large enough, experimentally determined features such as layer thickness, tilt angle, and degree of coverage can be accurately modeled.[10,11] But also in this approach size considerations are important. This becomes already apparent from observation of Figure 3: not all alkyl chains have precisely the same conformation on the surface, but several patterns occur. To sample all these patterns, a minimum number of around 30 alkyl chains (i.e., 60 $\equiv$Si–H groups) in the repeating box is required. Using this approach we were also able to approximate the optimum degree of coverage from the steric energy per chain (which includes both attractive and repulsive terms), and this number (50 %) is in excellent agreement with the experimentally observed values (50–55 %).[1,9] Since the accuracy of force fields continues to increase, molecular modeling via repeating boxes opens up the way to predict properties of functionalized monolayers, including those obtained from mixtures of alkenes (vide infra).

4. Functional Surfaces

The high stability of these covalently attached monolayers and the relatively mild conditions required for their formation allow the construction of functionalized silicon surfaces. In principle, two approaches can be taken: direct reaction of an ω-functionalized 1-alkene with a hydrogen-terminated surface, or reaction of a 1-alkene with a protected functional group at the ω-position. Since several functional groups that would be interesting for further conversion are themselves reactive towards hydrogen-terminated Si surfaces (e.g., –OH and –NH₂),[9] the latter approach is the most generally applicable one. This should specifically be taken in combination with the use of a mixture of ω-functionalized 1-alkenes with 1-alkenes without additional functional groups. In that case, the ω-functionalized 1-alkene yields the availability of receptor sites, while the unfunctionalized 1-alkenes take care of the formation of a dense and stable layer.

This approach hinges on the excellent stability of the Si–C bond, as this allows many reaction conditions to be used in conversion of the functional group at the ω-position. Examples of such conversions that keep the monolayer intact include the transesterification of alkyl monolayers under acidic conditions, and the reduction of an ester moiety to an alcohol by LiAlH₄ (see Fig. 5).[9] Given the rapid increase in computational possibilities for an accurate representation of such functionalized monolayers, the coherent experimental and theoretical study of such layers is bound to open up access to a wide array of monolayers with properties that can to a high degree be both controlled and predicted.
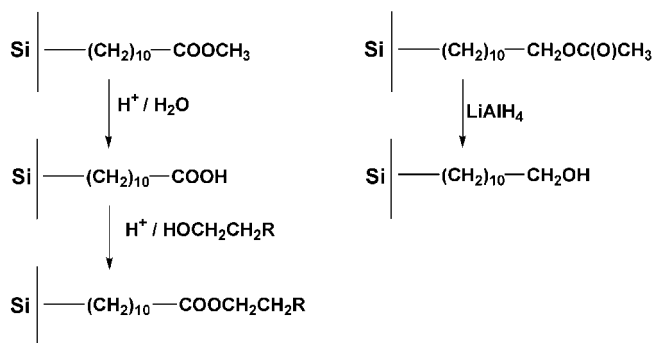
Fig. 5. Modifications of covalently attached monolayers.

5. Future Applications

At least three features of covalent monolayers on Si surfaces demand further investigation in the light of future applications.

First, the method of silicon surface modification using alkenes can be used in the surface passivation of Si solar cells. Upon irradiation of a photovoltaic Si solar cell, holes and electrons are formed that should be collected at opposite electrodes. A fraction of these holes and electrons, however, recombine, which reduces the overall efficiency of the solar cell. This recombination takes place in the bulk of the material and at the surface; for highly pure Si substrates, as used in solar cells, surface recombination is the dominant process. Attachment of a covalent monolayer reduces the number of available surface sites where recombination of electrons and holes can take place. The effective lifetime (τ_{eff}) of the free charge carriers was monitored using the modulated free carrier absorption method. Charge carriers are generated with an intensity-modulated 850 nm laser, while the concentration of charge carriers is probed with a second laser operating at 1550 nm. From these measurements τ_{eff} was determined to be 100–115 μs, compared to 5–7 μs of unpassivated Si wafers.[12] The obtained values for τ_{eff} of passivation by monolayer formation are similar to those obtained using other non-nitride passivation methods, such as iodine/ethanol treatment or the use of hydrogen-terminated silicon. Given the significantly increased stability of the surface compared to these two methods (months rather than minutes), and the reproducibility of the surface properties, covalent attachment of monolayers has definite advantages.

Second, the functionalization of monolayers allows the adsorption of species at the monolayer. This can be based on aspecific adsorption, such as present in the immobilization of polystyrene brushes at a styrene-derived monolayer.[13] A far more wide-ranging application would involve the specific adsorption of species at the surface, i.e., specific recognition at receptor sites (see Fig. 6). As binding yields molecular changes close to the (semiconducting!) Si surface, such specific recognition can form the basis of a new generation of highly sensitive silicon-based biosensors.

Third, the reaction of alkenes with a hydrogen-terminated silicon surface can also be performed under photochemical initiation (this was in fact Chidsey's original approach to obtain these layers[1]). This opens up the way for photopatterning of silicon surfaces, and the first example of such an approach has recently been reported.[14]
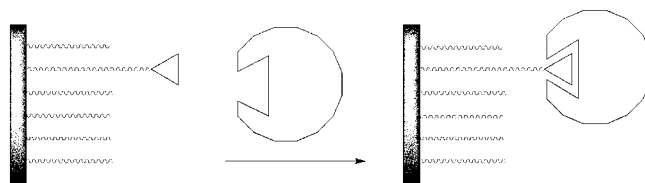

Fig. 6. Specific recognition of biomolecules on a functionalized covalent monolayer.

[1] a) M. R. Linford, P. Fenter, P. M. Eisenberger, C. E. D. Chidsey, *J. Am. Chem. Soc.* **1995**, *117*, 3145. b) M. R. Linford, C. E. D. Chidsey, *J. Am. Chem. Soc.* **1993**, *115*, 12 631.

[2] J. Terry, M. R. Linford, C. Wigren, R. Cao, P. Pianetta, C. E. D. Chidsey, *J. Appl. Phys.* **1999**, *85*, 213.

[3] M. M. Sung, G. J. Kluth, O. W. Yauw, R. Maboudian, *Langmuir* **1997**, *13*, 6164.

[4] a) E. Lukevics, *Russ. Chem. Rev. (Engl. Transl.)* **1977**, *46*, 264. b) J. L. Speier, *Adv. Organomet. Chem.* **1979**, *17*, 407.

[5] J. E. Bateman, R. D. Eagling, B. R. Horrocks, A. Houlton, *J. Phys. Chem. B* **2000**, *104*, 5557.

[6] a) A. B. Sieval, V. Vleeming, H. Zuilhof, E. J. R. Sudhölter, *Langmuir* **1999**, *15*, 8288. b) The first report of the use of dilute alkene solution is: J. E. Bateman, R. D. Eagling, B. R. Horrocks, A. Houlton, *Angew. Chem. Int. Ed.* **1998**, *37*, 2683. c) The use of toluene as solvent for monolayer preparation on porous silicon works well [6b]. On crystalline hydrogen-terminated surfaces (Si(100) and Si(111)) the study in [6a] showed mesitylene to be a superior choice for those surfaces.

[7] a) A review of the various methods has appeared: J. M. Buriak, *Chem. Commun.* **1999**, 1051. Recent papers using these methods include: b) J. M. Buriak, M. P. Stewart, T. W. Geders, M. J. Allen, H. C. Choi, J. Smith, D. Raftery, L. T. Canham, *J. Am. Chem. Soc.* **1999**, *121*, 11 491. c) A. Bansal, N. S. Lewis, *J. Phys. Chem. B* **1998**, *102*, 1067. d) A. Bansal, N. S. Lewis, *J. Phys. Chem. B* **1998**, *102*, 4058. d) R. Boukherroub, D. D. M. Wayner, *J. Am. Chem. Soc.* **1999**, *121*, 11 513.

[8] R. Boukherroub, S. Morin, F. Bensebaa, D. D. M. Wayner, *Langmuir* **1999**, *15*, 3831.

[9] A. B. Sieval, A. L. Demirel, J. W. M. Nissink, M. R. Linford, J. H. van der Maas, W. H. de Jeu, H. Zuilhof, E. J. R. Sudhölter, *Langmuir* **1998**, *14*, 1759.

[10] A. B. Sieval, B. Van den Hout, H. Zuilhof, E. J. R. Sudhölter, *Langmuir* **2000**, *16*, 2987.

[11] A. B. Sieval, B. Van den Hout, H. Zuilhof, E. J. R. Sudhölter, unpublished.

[12] A. B. Sieval, H. Zuilhof, E. J. R. Sudhölter, F. M. Schuurmans, W. C. Sinke, in *Proc. 2nd World Conference on Photovoltaic Solar Enery Conversion (Vienna 1998)*, European Commission, Ispra, Italy **1998**, p. 322.

[13] E. P. K. Currie, A. B. Sieval, M. Avena, H. Zuilhof, E. J. R. Sudhölter, M. A. Cohen Stuart, *Langmuir* **1999**, *15*, 7116.

[14] F. Effenberger, G. Gotz, B. Bidlingmaier, M. Wezstein, *Angew. Chem. Int. Ed.* **1998**, *37*, 2462.