DOI: 10.1002/anie.200500633

Self-Assembled Monolayers

Engineering Silicon Oxide Surfaces Using Self-Assembled Monolayers

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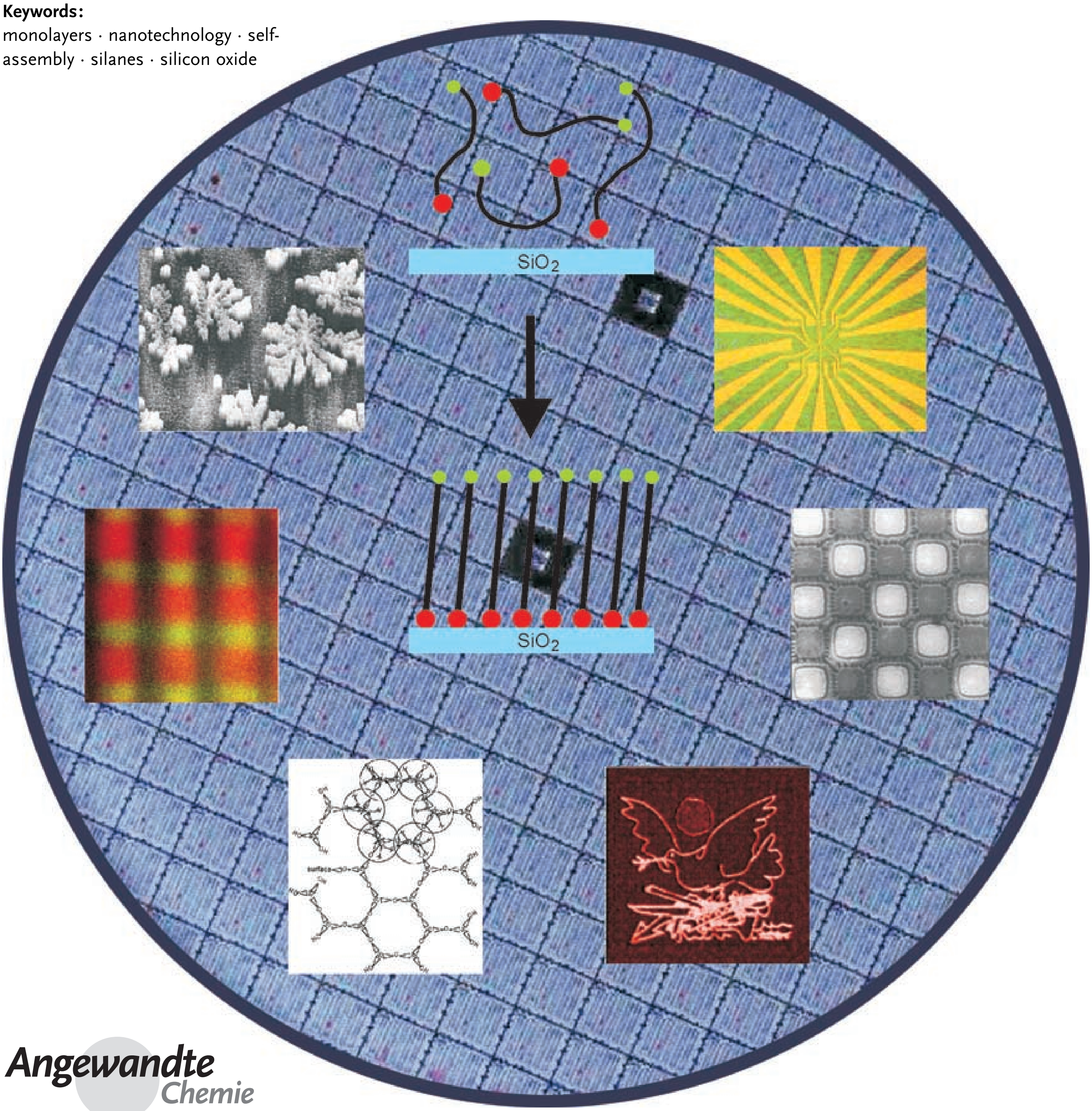
Keywords:
monolayers · nanotechnology · self-assembly · silanes · silicon oxide



Although a molecular monolayer is only a few nanometers thick it can completely change the properties of a surface. Molecular monolayers can be readily prepared using the Langmuir–Blodgett methodology or by chemisorption on metal and oxide surfaces. This Review focuses on the use of chemisorbed self-assembled monolayers (SAMs) as a platform for the functionalization of silicon oxide surfaces. The controlled organization of molecules and molecular assemblies on silicon oxide will have a prominent place in "bottom-up" nanofabrication, which could revolutionize fields such as nanoelectronics and biotechnology in the near future. In recent years, self-assembled monolayers on silicon oxide have reached a high level of sophistication and have been combined with various lithographic patterning methods to develop new nanofabrication protocols and biological arrays. Nanoscale control over surface properties is of paramount importance to advance from 2D patterning to 3D fabrication.

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1. Introduction

The term "self-assembling monolayer" was coined in 1983 in *New Scientist*[1] in an anonymous report describing the work of Lucy Netzer and Jacob Sagiv on the chemically controlled layer-by-layer self-assembly of multilayer films.[2] The self-assembly of adsorbates on an appropriate surface has been known since 1946, when Zisman and co-workers reported the formation of monomolecular films of long-chain hydrocarbons carrying polar groups on a variety of polar surfaces.[3,4] Although these films are extremely thin (typically ca. 2 nm), they are able to completely change the surface properties. However, the versatility of these adsorbed monolayers was not realized until 1978, when Polymeropoulos and Sagiv proposed their use for measuring electrical conduction between two metal surfaces.[5] In 1980, Sagiv published the first article demonstrating the formation of well-defined organosilane monolayers on SiO_2 by direct adsorption (that is, self-assembly) from solution.[6]

Self-assembled monolayers (SAMs) are highly ordered two-dimensional structures that form spontaneously on a variety of surfaces. Several reviews have discussed this subject.[7–10] The most common adsorbate/substrate combinations are alkylsilanes on oxide surfaces,[6] and sulfur-containing molecules on gold.[11] Although the latter combination has received the most attention, presumably because of the ease of preparation, alkylsilane monolayers on oxide surfaces such as SiO_2 possess some advantageous features. The covalent nature of the assembly process results in them displaying superior stability, which allows extensive handling and further modification steps without deterioration of the monolayer. Moreover, these SAMs are compatible with silicon technology and permit the use of optical techniques, such as fluorescence spectroscopy, as read-out methods.

Since the pioneering work of Sagiv and co-workers in the 1980s,[2,6,12–19] the field of SAMs on SiO_2 surfaces has grown exponentially. SAMs are not merely a method to passivate surfaces, but constitute ordered molecular platforms that can be employed in surface patterning and bottom-up nanofabrication techniques. However, in contrast to the increasing sophistication of the molecular architectures based on SAMs, the actual mechanism of monolayer formation remains a subject of debate. Many studies have been carried out to elucidate this process, but the results are often conflicting.

In this Review the mechanism of monolayer formation will be discussed, followed by an overview of the chemistry that has become available to derivatize monolayers. Much of this chemistry is exploited for applications, such as (bio)-chemical sensing. Particularly important for the application of SAMs in areas such as nanotechnology and biological array formation has been the development of (soft) lithographic methods, which can be used to address and modify selected parts of the surface in a controlled manner. These methods greatly facilitate the preparation of high-density chemical patterns on a surface, which in turn are available for further functionalization by, for example, self-assembly. In this way, SAMs form well-defined platforms for nanofabrication, where a 2D pattern is expressed and amplified in a 3D functional structure. An overview of the techniques available for surface patterning is presented and future applications of SAMs are discussed.

2. Self-Assembled Monolayers on Silicon Oxide

The development of analytical tools for the study of SAMs has been impressive in the last two decades. The methods that are used most frequently are listed briefly here. It should be

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noted that a satisfactory characterization of films with a thickness of just a few nanometers can only be obtained by combining several of these techniques, each providing specific information. Contact angle goniometry provides information on the polarity, roughness, and order of a SAM.[7] Ellipsometry is a common optical technique for the determination of the thickness of thin films.[7,20] Detailed information on the elemental composition of SAMs can be gathered by X-ray photoelectron spectroscopy (XPS),[21] which probes the kinetic energy of the inner or valence electrons ejected by an incident photon with a known energy $h\nu$. An alternative technique to study the composition of a monolayer is secondary ion mass spectrometry (SIMS).[22,23] SIMS uses a beam of high-energy "primary" particles (ions) to bombard the SAM and analyses the ionized "secondary" particles that are emitted. Fourier transform infrared spectroscopy (FT-IR) can be employed to determine the molecular packing and orientation as well as to identify functional groups in SAMs.[22] It is mainly used in three spectroscopy modes: attenuated total reflection,[24] grazing angle,[25] and Brewster angle.[25] The electron-density profile of thin films can be probed by X-ray reflectivity, which can be used to determine the film thickness.[26] The technique of choice to measure surface topology, nanoscale structures, and molecular as well as atomic scale lattices is atomic force microscopy (AFM),[27] which measures the repulsive and attractive forces between a very sharp tip (radius 10–100 nm) and the sample surface.

2.1. Mechanism of Formation

There has been considerable debate on how SAMs are formed on SiO_2. Especially in the late 1980s and 1990s, when the field started to grow rapidly, many fundamental studies were performed to establish a clear picture of the mechanism of monolayer formation and to formulate procedures that would guarantee reproducibility. It soon became apparent that several parameters are important in monolayer formation and, in particular, the role of water has been investigated thoroughly. The first SAM of octadecyltrichlorosilane (OTS) molecules was reported by Sagiv.[6] He recognized that water adsorbed on the surface was necessary to hydrolyze the chlorosilane and assumed that the hydrolyzed molecules would undergo condensation reactions with the surface hydroxy groups[28] and other OTS molecules to form a polymerized network of molecules in which each OTS molecule is covalently anchored to the surface.

This view on the self-assembly process had to be adjusted when Finklea et al. discovered that organized monolayers of OTS could also be formed on a gold surface, that is, a surface devoid of hydroxy groups.[29] They concluded that self-assembly occurs on the adsorbed water film on the gold substrate and that the silane head groups are incorporated into a two-dimensional cross-linked network of Si-O-Si bonds. This view was later confirmed by Allara et al.[30] The observation of a lower roughness of silanized wafers compared to unmodified wafers, as observed in X-ray reflectivity experiments by Silberzan et al., also indicated that not all molecules are individually linked to the surface, but rather form a cross-polymerized network of molecules with only a few bonds to the surface.[31] This scenario was supported by the IR studies of Tripp and Hair:[32,33] they found in a low-frequency IR study that the adsorbed species form few, if any, Si-O-Si bonds with the surface.

Commonly, the surface is activated prior to the self-assembly to clean the surface and maximize the number of silanol groups at the surface.[28] There are several methods to achieve this, but usually strong acids or an oxygen plasma are employed. This procedure renders the surface hydrophilic and prone to the formation of a thin water layer. There is a general consensus that trace amounts of water are essential for the formation of well-packed monolayers. Several studies even reported that the quality of SAMs increases with the degree of hydration of the substrate.[24,32,34–36] SAMs formed on dry SiO_2 surfaces are generally of poor quality. IR data suggested that a uniform film containing disordered alkyl chains was formed.[24] Tripp and Hair showed that a solution of OTS in carbon tetrachloride does not react at all with the surface in the absence of moisture.[32,37] Rye et al. compared the saturation coverage of octadecyldimethylchlorosilane (ODMS) and OTS.[38] The ODMS coverage on hydrated surfaces was approximately one third of the OTS coverage. In contrast, when the substrates were vacuum-baked prior to self-assembly the saturation coverages were comparable. Rye et al. attributed this to coupling reactions being limited to the surface hydroxy groups.

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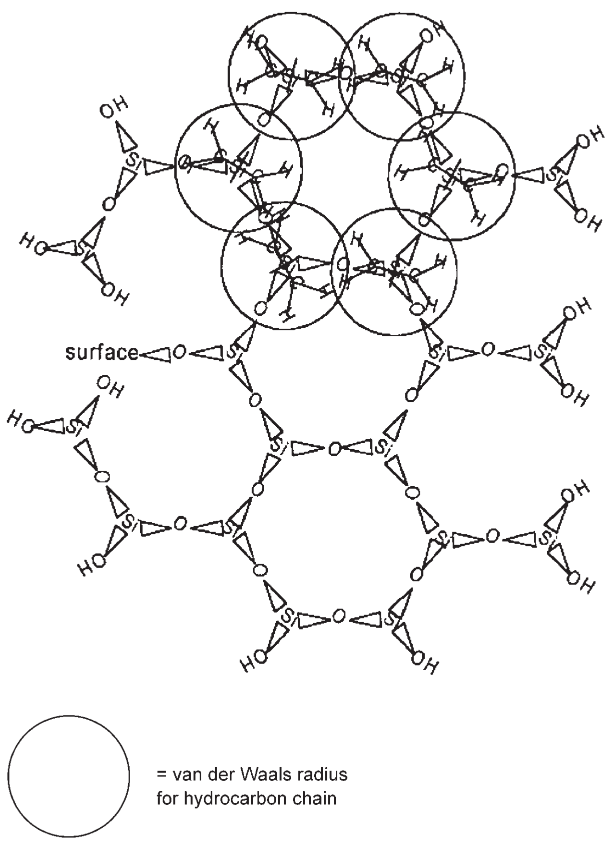

Figure 1. Model of a growing monolayer crystallite resulting from the reaction of an alkyltrichlorosilane with a silicon oxide surface.[39]

The same authors proposed a model of a growing crystallite resulting from the reaction of an alkyltrichlorosilane with oxidized silicon covered by a thin water layer.[38,39] The model, shown in Figure 1, is controversial. The model shows alkyl chains that are forced into proximity by the covalent bonds of the Si-O-Si framework and not by the interaction of the alkyl chains. A distance of 3.5 Å between nearest neighbor Si atoms was used in the construction of the model and the circles around the hydrocarbon chains represent the van der Waals radius for linear hydrocarbons (2 Å). Rye et al. claimed that the steric crowding imposed on the alkane chains can be reduced by a tilt of the chains relative to the surface normal. However, in a modeling study by Stevens it was shown that cross-polymerization, which was considered an essential element in the formation of stable SAMs on SiO_2, cannot occur for monolayers at full surface coverage.[40] The reason for this is because of steric effects.

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A fundamental inconsistency in the organization in a monolayer as proposed in Figure 1 is that the covalent bonds in the Si-O-Si network (3.2 Å) are substantially shorter than the van der Waals diameters for C atoms (3.5 Å). The steric overlap is even larger when the hydrogen atoms of the hydrocarbon chain are also taken into account. Moreover, complete cross-polymerization would yield an area per chain of around 11 $Å^2$, which is not possible and not observed. Instead, the experimentally observed area per chain of 21–25 $Å^2$[26,41–45] is more consistent with the area per chain of 20–24 $Å^2$ that was found for hexagonally close-packed Langmuir–Blodgett layers of OTS,[46,47] thus indicating that SAMs on SiO_2 are very similar to Langmuir–Blodgett layers.

Kajiyama and co-workers compared OTS monolayers prepared by the Langmuir–Blodgett method and the chemisorption method,[48] and found that OTS molecules in the Langmuir monolayer were less tilted (ca. 8–10°) than in the chemisorbed layers (15–17°). The Langmuir monolayers are also slightly better ordered, as concluded from the spacing of the molecules. The molecular packing of chemisorbed monolayers was discussed earlier.[49] Taking into account the overall experimental evidence furnished by IR and X-ray scattering data collected strictly from the same film specimens, they proposed a dynamic structural model that can reconcile the steric limitations imposed by the packing of perpendicularly oriented hydrocarbon tails with the apparent formation of extended lateral siloxane (-Si-O-Si-O-) chains. More recently, further evidence in support of this model was put forward in a semiquantitative experimental evaluation of the intra- and interlayer modes of bonding in organosilane multilayers.[50] The hydrocarbon chains in these highly ordered multilayers adopt an essentially perpendicular orientation (that is, no significant tilt) with a maximum molecular area of 20 $Å^2$. Thus, it seems reasonable to conclude that SAMs of alkylsilanes on SiO_2 are very similar to Langmuir–Blodgett layers and that the reduced ordering of the SAMs can be explained by a certain degree of cross-polymerization. This most likely accounts for the fact that no long-range order is observed.

Recently, Wang et al. reported a method to grow ultrasmooth OTS monolayers on native SiO_2.[51] By comparing the deposition of OTS under "dry" and "wet" conditions, they concluded that growth occurs by different mechanisms. In dry, hydrophobic solvents, when water is only present as a thin layer on the surface and not in solution, true monolayers could be grown with a root-mean-square roughness of about 1 Å in two days, which is a much longer deposition time than usually applied. Under "wet" conditions OTS condensed into flat aggregates in solution which subsequently adsorbed onto the substrate. Since the aggregates are preformed in solution, they cover the substrate much faster than under "dry" conditions, but are not able to form a smooth monolayer.

The role of solvents on the self-assembly process was systematically investigated by McGovern et al.,[52] and by Hoffmann et al.[20] McGovern et al. found that aromatic solvents such as toluene, which are able to extract significant amounts of water from the substrate, yielded the densest OTS films in one hour and postulated that hydrolysis of OTS took place in solution rather than at the surface, as had commonly been assumed until then. In the second study, kinetic information on the monolayer growth in different solvents was obtained by in situ ellipsometry measurements. Different solvents resulted in differences in the rate of monolayer growth of up to a factor of 50.

The study of partially formed monolayers is helpful to understand the self-assembly process and was a topic of controversy during the 1980s and early 1990s. Sagiv and co-workers proposed that monolayers are formed through islands, as suggested by IR data on partially formed SAMs,[14,17] while others concluded that disordered, homogeneous, but incomplete monolayers are formed.[26,42,53–55] Both processes are illustrated in Figure 2.

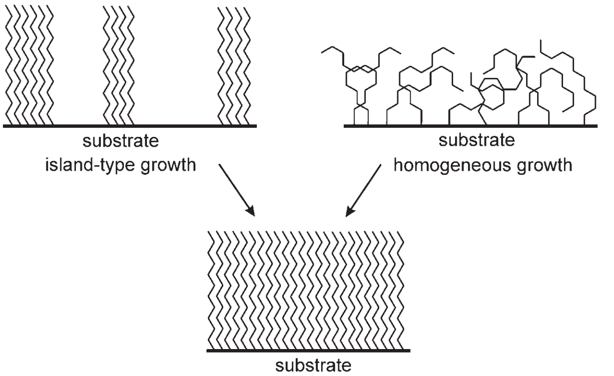


Figure 2. Schematic representation of island-type growth and homogeneous growth of SAMs.

Eventually, it was shown by AFM that OTS monolayers grow via islands that are virtually perpendicular to the substrate surface.[56] Perfluorinated trichlorosilanes also grow via island formation,[57] and alternate phases depending on the deposition conditions.[58] In contrast, shorter-chain molecules do not show island growth.[56] Several AFM studies revealed that the deposition process strongly depends on parameters such as solvent,[59] solution age,[60–62] water content,[51,60,61,63] deposition time,[62–64] and temperature.[65–68] Vallant et al. observed both homogeneous growth and island-type growth depending on the water content and age of the silane solution.[60] Island-type growth was found to be strongly favored with increasing water content or age of the solution. This result is indicative of the formation of larger preorganized aggregates of siloxanes in solution. However, Wang and Lieberman recently showed that even in the absence of traces of water in solution, the self-assembly process still proceeds via island-type growth.[51] The reason that this was not observed in other studies is probably the slow kinetics. Wang et al. claim that they observed monolayer islands after 18 h of deposition time in the absence of water, while deposition times of only seconds to a few hours are common. Figure 3 shows a tapping-mode AFM image of a partial OTS film on oxidized silicon, which clearly shows the growth of an OTS monolayer via islands.

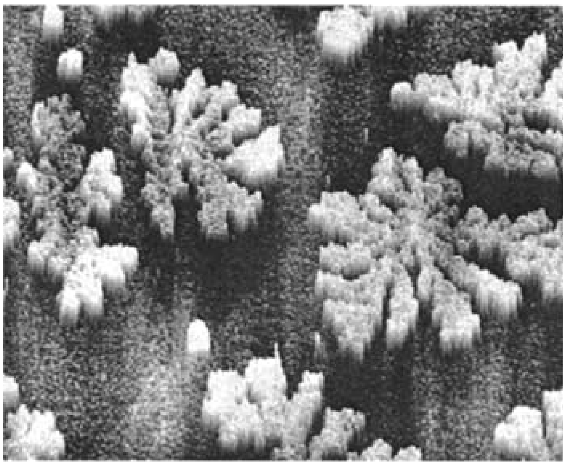


Figure 3. Tapping mode AFM image (20×20 μm^2) of a partial OTS film on oxidized silicon.[67]

The formation of monolayers appears to proceed through a number of stages. A combined lateral force microscopy (LFM) and sum-frequency generation (SFG) spectroscopy study by Liu et al. showed OTS adsorption from solution and the beginning of island formation during the initial stage. This process was followed by a dramatic change in the conformation of the alkyl chain within the film from a disordered to an ordered, mainly all-*trans* conformation, with only a small increase in surface coverage.[63] The final stage is a much slower adsorption process to form a complete monolayer. Balgar et al. observed two regimes: a nearly linear growth up to a coverage of about 75 %, followed by slow saturation at higher coverages.[64]

Despite the complex mechanism of monolayer formation, and its dependence on many parameters, several studies reported first-order Langmuir adsorption kinetics by using analytical techniques such as in situ attenuated total reflection infrared spectroscopy (ATR-IR),[69] in situ AFM,[61] X-ray reflectivity,[70] and in situ ellipsometry.[20] Recently, a simple two-dimensional model for the growth of alkylsilane monolayers on hydroxylated surfaces was proposed.[71] The model, which takes into account the weak and strong bonding interactions of the aggregating species, was able to reproduce characteristics such as island-type growth and first-order Langmuir adsorption kinetics. In addition, it provides an explanation for the observed deviations from the first-order Langmuir adsorption kinetics in various ex situ studies.[64,72]

The observation that monolayer formation depends on temperature was reported in the very first paper on monolayer self-assembly.[3] A thorough account reporting the existence of a critical temperature above which monolayers are not produced followed as early as 1947, in the second classic paper published by Zisman and co-workers on the formation of such monolayers.[4] These observations were "rediscovered" 45 years later by Silberzan et al.[31] who also found that lower temperatures favor the chemisorption, which may seem paradoxical at first sight. Several research groups have studied this phenomenon by monitoring the surface tension and confirmed that a critical temperature, close to ambient temperature for OTS, exists for the formation of high-quality SAMs.[73–75] As the critical temperature was found to depend on the length of the alkyl chain, these studies related the critical temperature to the triple point observed in the phase diagram of Langmuir layers at the air–water interface. Silberzan and co-workers confirmed the analogy to Langmuir films by AFM studies.[65,72] Island-type growth takes place below the critical temperature, while islands were not observed for depositions above the critical temperature. However, Rye reported that a much simpler and more straightforward correlation exists between the melting points of alkanes and the observed critical temperature.[39]

Time-resolved AFM studies by Carraro et al. indicated three distinct mechanisms, depending on deposition temperature: island growth at low temperatures, homogeneous growth at high temperatures, and a mixed regime at intermediate temperatures.[66] Later, they reported an experiment that showed reversible structural change of the same partial OTS monolayer as a function of temperature at constant coverage.[67] They concluded that the highly mobile monolayer exists in a hydrogen-bonded state at the surface and is closely related to the equilibrium state of Langmuir films at the air–water interface.

Recently, the interplay between water and temperature on the growth of OTS submonolayers was investigated.[76] Dynamic light scattering studies revealed the formation of aggregates in solution with a hydrodynamic radius of approximately 200 nm for all examined water concentrations and temperatures. However, formation of the aggregates was faster at higher water contents and lower temperatures. In addition, a characteristic temperature was found above which such aggregates could no longer be detected, and which was higher for higher water concentrations.

2.2. Stability of the Self-Assembled Monolayers

Part of the attractiveness of SAMs on SiO_2 stems from their stability, which is a vital issue in applications. The stability is caused by partial in-plane cross-linkage of the molecules and possible covalent anchoring to the substrate. SAMs of OTS are stable in air up to about 150 °C,[17,77–80] after which irreversible changes occur in the monolayer structure. Perfluorinated SAMs appear to be even more resistant towards thermal decomposition:[78,81] Srinivasan et al. reported that $1H,1H,2H,2H$-perfluorodecyltrichlorosilane coatings remain intact even up to 400 °C.[78] The stability toward various chemicals is also remarkable: OTS SAMs can be washed with organic solvents, hot (tap) water, or detergent solutions without detectable damage to the layer.[82,83] Their stability in boiling solvents such as chloroform and water is good,[84] but when exposed to 2.5 M sulfuric acid in boiling dioxane or 48 % aqueous HF the layers were damaged significantly, as witnessed by reduced ellipsometric thicknesses.[85] Wasserman et al. found that exposure of tetradecyltrichlorosilane SAMs to 0.1 N HCl for more than 40 h did not affect the monolayer, but immersion in 0.1 N NaOH resulted in immediate degradation.[86] This lack of stability in basic media was attributed to the hydrolysis of Si–O bonds close to the surface.

One of the first applications where SAMs on SiO_2 were thought to play a key role was in boundary lubrication in, for example, magnetic storage devices. As early as in 1993, the tribological properties of alkylsilane films on solid substrates were investigated.[87] The friction of coated interfaces was lower compared to the friction of bare interfaces, and the lifetime of the lubricated interfaces increased with increasing chain length.[87,88] Srinivasan et al. examined the potential of SAMs for the reduction of adhesion in microelectromechanical systems.[78] They found a reduction in adhesion by more than three orders of magnitude upon applying an OTS coating, while fluorinated SAMs reduced it further by a factor of four. The mechanical strength of octadecyltriethoxysilane (OTE) layers on mica has been investigated by scratching studies with an AFM tip.[89] No mechanical wear was observed for loads up to 300 nN when a large tip radius was used. When sharper tips were used a load of about 10 nN was sufficient to displace the OTE monolayer. *n*-Alkanethiols on Au were removed with a smaller force (ca. 5 nN) using the same sharp tip. However, a more recent study questioned the mechanical stability of OTS SAMs on SiO_2.[90] Lower friction coefficients for monolayer-coated surfaces were reported, as well as a poor load-carrying capacity and antiwear ability. This report concluded that OTS SAMs could only be potential boundary lubricants at low loads.

3. Chemical Diversity of Self-Assembled Monolayers on Silicon Oxide

SAMs on SiO_2 provide molecularly defined platforms for chemical derivatization. Potential applications range from the control of surface properties to the fabrication of sensors and biochips as well as their use in nanotechnology. Progress in the development of these fields partly depends upon the ability to functionalize SAM surfaces with suitable groups. Two constraints determine the utility of SAMs on SiO_2 for the creation of functionalized surfaces: 1) the range of functionalities that can be tolerated in the self-assembly process to yield stable and ordered SAMs, and 2) the scope of chemical modifications of the monolayer that can be achieved.

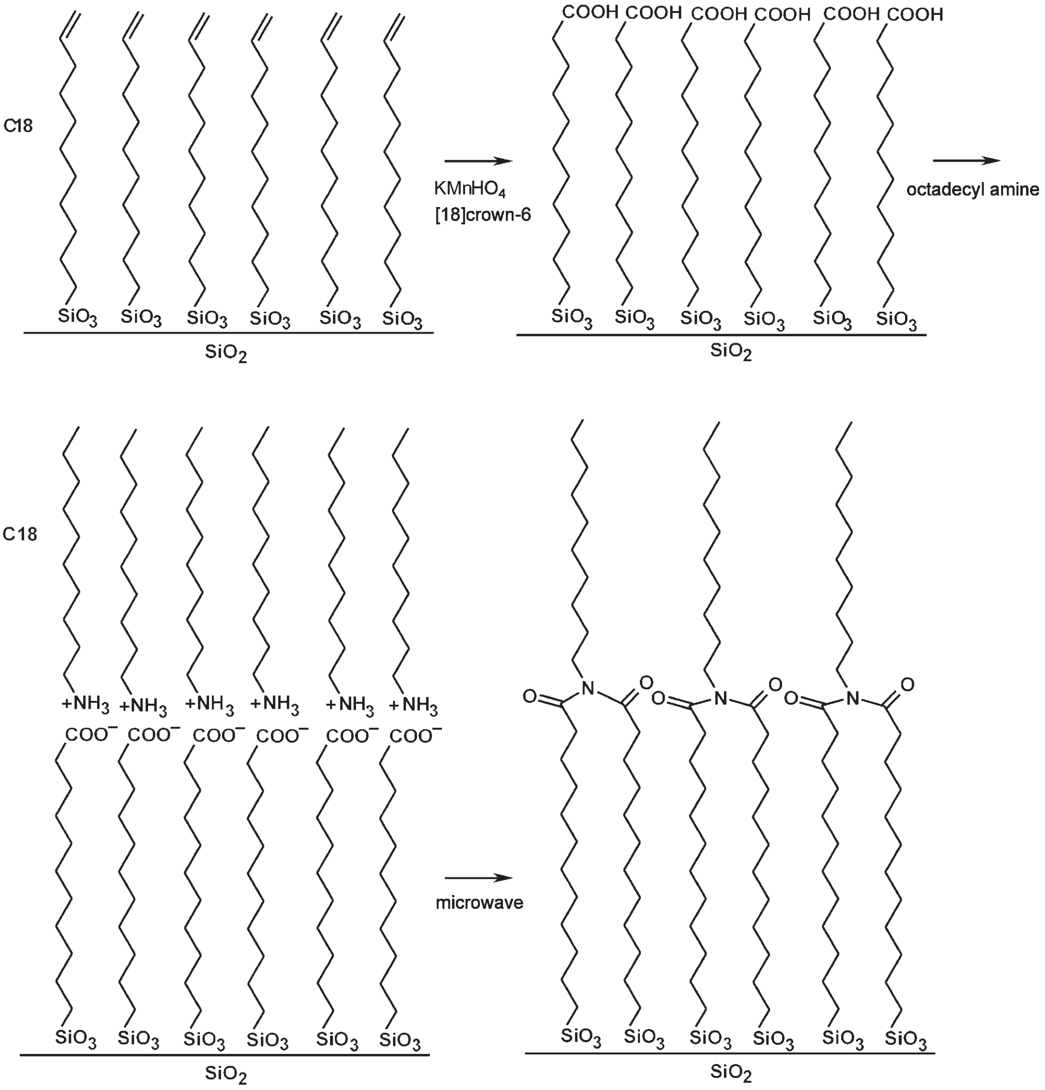
An efficient reaction in solution is not necessarily successful on a solid substrate. The reactivity of immobilized reactants can be significantly reduced as a consequence of steric constraints, transport limitations, solvation effects, charge, and dipole effects.[91] Therefore, the extent of reaction in a SAM depends strongly on the location of the reaction center: When it is located on the incoming reagent, the transition state does not experience much steric limitation, while if it is confined to the surface the reaction center is severely crowded by immobilized neighbors. Acid/base properties of surface-confined molecules can also differ significantly from those in solution.[92–95] Important factors might be the polarity of the surface, interfacial electrostatic fields, and the local structure of the solvent.

3.1. Self-Assembly of Functionalized Alkylsilanes and Chemical Transformations at the Monolayer Surface

The most straightforward way to prepare a functionalized SAM is by using an ω-substituted alkylsilane. In general, chlorosilanes are preferred over alkoxysilanes since they are more reactive. However, the reactivity of chlorosilanes severely limits the range of functional groups that can be introduced in this manner. The preparation of ω-functionalized alkyltrichlorosilanes is facilitated by using trialkoxysilanes as synthetic intermediates, as was reported by Barness et al.[96] These offer superior stability with respect to synthetic operations and can be converted into trichlorosilanes by reaction with trichloroacetyl chloride.

The first functionalized SAM was reported by Netzer and Sagiv, and contained vinyl groups that could be transformed into terminal hydroxy groups by hydroboration and oxidation.[2] Other reactions on these layers generated carboxylic acid, and bromo-terminated films.[86] A nice example of surface chemistry with these carboxylic acid monolayers was shown by Sagiv et al.[97] The carboxylic acids were used to form a bilayer with octadecylamine through electrostatic/hydrogen-bonding interactions. Exposure of the bilayer to microwaves resulted in the formation of imides (Scheme 1).

More recently, vinyl SAMs have been covalently coupled to zwitterionic phosphorylcholine groups.[98] Such monolayers are biocompatible and prohibit the deposition of enzymes and proteins. In addition, vinyl monolayers can be modified with adenine, and subsequently zeolite crystals functionalized with thymine were assembled at that surface through adenine–thymine hydrogen bonding.[99] Tillman et al. prepared monolayers incorporating phenoxy groups and methyl esters, of which the latter were reduced to the corresponding alcohols by $LiAlH_4$.[82,83,100] Other functional groups incorporated into monolayers include methyl ether,[101] acetate,[101] thiocyanate,[102] α-haloacetate,[103] (trimethylsilyl)ethynyl,[104] and thioacetate,[102] which can be reduced to thiols.[105]



Scheme 1. Microwave-induced imide formation in SAMs.[97]

A convenient starting point for chemistry on monolayers is provided by bromo-terminated SAMs.[69,101,106,107] Bromides can be quantitatively replaced by azide groups, which in turn are reduced to ω-amino SAMs,[102,108] or can be used to tether to a fullerene molecule.[109] In addition, bromides have also been replaced by other anionic nucleophiles such as thiocyanate and thiolate.[110] These reactions did not go to completion, most likely because of steric congestion and because thiocyanates and thiolates are less nucleophilic than azides.

An alternative method to obtain amino-terminated SAMs is by self-assembly of cyanide monolayers.[69,102] These SAMs can be reduced in one step using $LiAlH_4$ or BH_3.[102] Such amino-terminated SAMs form an important platform for reaction with functionalized molecules. Ordered and well-defined layers are obtained when amino-terminated SAMs are prepared by reduction of azides or cyanides.[102,108,111] Aminosilane films prepared in one step, on the other hand, are completely disordered.[112] XPS and IR measurements indicated that this is probably a result of interaction of the amino group with the SiO_2 surface.[112,113] Nevertheless, aminosilanes, and particularly 3-aminopropyltrialkoxysilanes (APS), have been used extensively as adhesion promoters and the well-known reactivity of amines has been exploited for the introduction of various functionalized molecules. APS layers were used to covalently bind fullerenes,[114,115] chromophores,[116,117] and fluorophores,[118,119] and to coordinate to a zinc porphyrin.[120] In addition, photoresponsive spiropyran molecules were covalently attached to an APS layer and used to induce reversible changes in wettability upon switching to a more polar zwitterionic merocyanine isomer, triggered by the absorption of UV light.[121,122] Other reactions on amino-terminated SAMs will be discussed in Sections 3.3 and 3.4.

SAMs exposing sulfanyl groups are potentially interesting because of their ability to coordinate to noble metals. The self-assembly of (mercaptopropyl)trimethoxysilane (MPTMS) has been reported,[91,123] and the preparation of colloidal gold multilayers using MPTMS as a linker molecule has been investigated.[124] This layer-by-layer growth method yields uniform colloidal Au multilayers. More recently, MPTMS layers have been oxidized to produce sulfonic acid functionalized silica that can be used as a catalyst in esterification reactions,[125] and MPTMS monolayers have also been used for electroless plating of Ag.[126]

Homogeneous epoxy-terminated SAMs have been reported by Luzinov et al. to serve as templates for the chemical tethering of polymer layers.[127] These layers can serve as functionalized surfaces and react with various amino-derivatized molecules. Kulak et al. attached an APS layer to zeolite crystals and found that the modified crystals assembled as monolayers on an epoxide SAM.[128] The zeolite layer remained intact after sonication, thus indicating that strong linkages were formed between each crystal and the substrate. Furthermore, epoxide layers were used to immobilize per-6-amino-β-cyclodextrin on SiO_2, which led to a surface exposing host molecules.[129]

The immobilization of polymers at a surface is a convenient way to tailor the surface properties of inorganic materials. One way to accomplish this is by the immobilization of initiators for the in situ generation of grafted polymers. Rühe and co-workers prepared layers of polystyrene and a perfluorinated polymer in a controlled manner and with high graft densities by using SAMs carrying azo initiators.[130,131] A particular interesting development in this area has been the use of a "living" free-radical process at the surface to prepare accurately controlled polymer brushes.[132–135] Advantages of this "living" polymerization include the control of molecular weight and polydispersity and the wide variety of monomers amenable to the process. In this way, surface-attached block and random copolymers can be formed for applications such as the precise tuning of surface properties and the preparation of responsive surfaces.[133,135]

Tailoring surface properties using SAMs does not necessarily require polymers. Surfaces with very low surface free energies are generated by self-assembly of fluorinated silanes,[57,101,136,137] while poly(ethylene glycol)-carrying silanes are widely used to prepare SAMs that resist the nonspecific adsorption of biomolecules.[138–140]

3.2. Formation of Multilayers

Whereas a SAM is only a few nanometers thick, many practical devices require the formation of high-quality, close-packed, and highly ordered films with thicknesses of a few hundred nanometers to several micrometers.[83] The growth of highly ordered multilayers is necessary to extend the two-dimensional structure of SAMs to the third dimension. Multilayer formation was studied for the first time by Netzer and Sagiv.[2] They described the conversion of an olefin-terminated SAM into a hydroxy-terminated surface, which could be used to deposit a second layer of olefinic silanes. However, hydroboration of the olefin was not quantitative and led to increasing disorder in the subsequent layers. An improvement of this strategy was reported in which the reduction of methyl esters to alcohols by $LiAlH_4$ was used,[83] which led to the construction of ordered assemblies of up to 25 discrete monolayers. A methodology to produce hydroxy-terminated siloxane-anchored SAMs and multilayers, which takes advantage of the photolysis of a nitrate-functionalized SAM for the formation of surface hydroxy groups without any reagents, was later reported.[141] This photoconversion allowed the photopatterning of films and subsequent construction of multilayers.

An alternative procedure to yield multilayer assemblies involves the immobilization of a boronate-protected trichlorosilane, which can be hydrolyzed conveniently with water/ethanol to a diol, after which the process can be repeated.[142] A different approach, reported by Yam and Kakkar,[143] involved acid-base hydrolysis of aminosilanes with dihydroxy-terminated molecules. The layer-by-layer construction methodology used $Si(NEt_2)_4$ and rigid, rodlike diols, and led to relatively close-packed multilayered structures.

Hydrogen bonds can also be used instead of covalent coupling to stabilize the three-dimensional structure of the multilayer. Maoz et al. oxidized an olefinic SAM to the corresponding carboxylic acid before the next silane layer was assembled on top.[49,144,145] Lateral cross-coupling of the silane head-groups provided structural robustness and a self-healing capability to the films. Noncovalent multilayers were also reported by Mallouk and co-workers.[146,147] They used the strong electrostatic and coordinative interaction between phosphonates and Zr^{4+} ions for the formation of multilayers.

Marks and co-workers prepared thin-film nonlinear optical (NLO) materials consisting of self-assembled chromophore-containing multilayer structures.[148–154] They reported the formation of an acentric monolayer by self-assembly of a trimethoxysilane-functionalized azobenzene chromophore from solution. A siloxane capping layer was subsequently formed, which stabilized the structure by cross-linking and provided hydroxy groups to start a new cycle (Figure 4). The advantages of this approach to prepare NLO materials are the high chromophore concentration of the SAM and its robustness as a consequence of the covalent bonds.

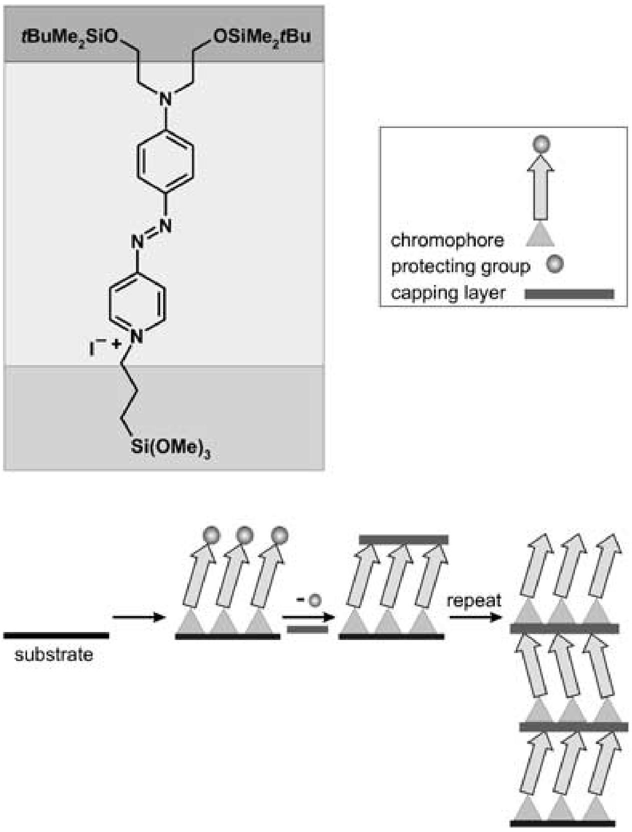


Figure 4. NLO materials obtained by self-assembly of chromophoric superlattices.[154] Self-assembly of the chromophore yields a hydrophobic surface. Treatment with octachlorotrisiloxane ($Si_3O_2Cl_8$) results in deprotection and in the formation of a robust polysiloxane capping layer approximately 0.8 nm thick.

3.3. Sensor Layers

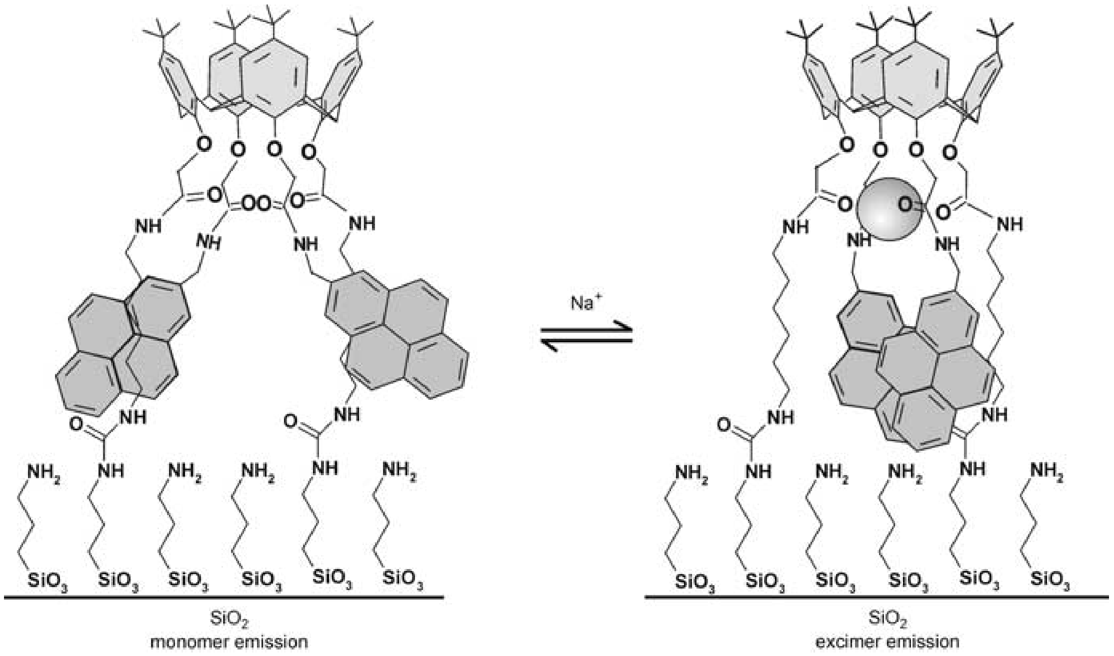
One field of increasing interest in which SAMs are employed extensively is (bio)chemical sensing. Immobilization of sensor systems implies the transition from solution to the solid state, which offers a convenient way to couple sensing systems to the macroscopic world through read-out functions. Furthermore, immobilized sensors usually have faster response times, are easier to handle, and may be recycled. Most sensor functionalities in SAMs were developed for gold surfaces, with read-out techniques such as electrochemistry, surface plasmon resonance, and AFM.[25]

Fluorescence spectroscopy has advantages over electrochemical methods, as there is no need for reference electrodes or additional electrolytes.[155] Moreover, molecules labeled with fluorescent probes are easily prepared or commercially available and can even be visualized individually. Fluorescence spectroscopy is extensively used in biological sensing (see Section 3.4), where it is applied in, for example, DNA chips and protein microarrays to gain information at the nucleic acid or protein level. The reason for the limited use of fluorescence spectroscopy on gold lies in the strong quenching effect of the gold substrate on the fluorescence of nearby molecules,[156] thus making oxide surfaces such as SiO_2 the surface of choice for the immobilization of fluorescent sensing molecules.[157–161]

One of the first immobilized sensors was reported by de Silva et al.[162] The sensor consisted of an anthracene fluorophore covalently connected to an APS layer. The fluorophore could behave as a pH probe depending on the protonation state of the amino group. Porphyrins linked to an APS layer were reported by McCallien et al.[163] After attachment to the substrate, zinc was inserted and the interaction of the zinc porphyrins with amino ligands was investigated by UV/Vis spectroscopy. Porphyrins could also be immobilized through reaction of a vinyl or hydroxyethyl group of a porphyrin with a sulfanyl-terminated monolayer, thus providing a simple and direct method for attaching porphyrins on solid substrates.[164] UV/Vis measurements were used to monitor the coordination of carbon monoxide to various metal porphyrins.

Sensing by host–guest interactions on the SiO_2 surface has been reported by several research groups. Fullerenes were attached to silica gel to investigate binding affinities of potential hosts such as calixarenes and cyclodextrins.[165] Cyclodextrins (CDs) constitute a class of receptor molecules that have been studied extensively in solution. CD films were prepared to monitor the interactions with various guest molecules,[129,166,167] and in an elegant experiment Flink et al. monitored the interaction of β-CD hosts with monolayers of dansyl adsorbates by polarity-dependent fluorescence.[168] Recently, we reported a procedure that yields densely packed β-CD monolayers, and it was shown that the binding properties of the CDs were retained when they were assembled at a surface.[111] A monolayer bearing preorganized binding sites for metal ions was reported by van der Veen et al. (Scheme 2).[155] They used a calix[4]arene receptor modified with ligating groups and two pyrene fluorophores. The immobilized receptor site showed selectivity for Na^+ over other alkali-metal ions. The complexation of Na^+ ions could be monitored by a decrease in monomer emission and an increase in excimer emission.

Although the fluoroionophore shown in Scheme 2 was found to be a good receptor for Na^+ ions, the use of preorganized recognition sites brings forth certain disadvan-



Scheme 2. Immobilized Na^+-selective fluoro-ionophore which shows a change from the monomer emission to excimer emission upon complexation of Na^+ ions.[155]

tages: It requires lengthy syntheses and results in disordered monolayers as a result of the bulkiness of the receptor molecule. Therefore, a new approach was developed more recently.[169,170] It relies on the immobilization of ligating functionalities on an amino-terminated SAM, without any preorganization. A small library containing various simple ligating and reporter molecules was made, and the response to different metal ions was measured. The results showed that selectivity for different metal ions depended on the surface functionalization. The same approach was used by Brasola et al. to develop a fluorescence nanosensor for Cu^{2+} ions on silica particles, the only difference being the immobilization of ligating and reporter molecules in one step, instead of linking them to a preformed monolayer.[171]

3.4. Immobilization of Biomolecules

The attachment of biologically active molecules to surfaces is of considerable importance for the development of biological microarrays, such as DNA chips and protein microarrays.[172,173] DNA chips are promising for obtaining information on nucleic acid levels and sequences in a fast, simple, and cheap way, and are developed for use in large-scale genotyping and gene-expression profiling.[172] Protein microarray technology is valuable in the pharmaceutical industry for the acceleration of drug target and diagnostic biomarker discovery.[173] Crucial to the development of these small-molecule microarrays is the ability to selectively attach molecules to the surface under mild conditions and at the same time avoid nonspecific interactions. Moreover, the reactions should be compatible with a wide variety of functional groups that occur in biologically relevant molecules. To meet these requirements, extensive research has been performed to expand the immobilization techniques on surfaces. Recently, an overview of different reactions that have been studied with monolayers on Au and SiO_2, with the emphasis on immobilization of biomolecules, was reported.[174]

The formation of amine-terminated SAMs on glass surfaces allows immobilization of biologically important molecules in both a covalent and a noncovalent way. Cells stick to the SAMs through electrostatic interactions between the positively charged ammonium groups and the negatively charged cell membrane.[175] This simple electrostatic adsorption has also been used to link short oligonucleotides to a positively charged amino-functionalized SAM.[176] This method produced a stable oligonucleotide monolayer with a density that approached a two-dimensional close-packed array.

Several mild methods have been developed to covalently couple biological molecules to the glass surface. Successful reactions include *N*,*N'*-dicyclohexylcarbodiimide (DCC) coupling of pepsin,[91] 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (EDC) coupling of DNA,[177] the immobilization of *p*-nitrophenyl chloroformate activated dextrans,[178] reaction of compounds containing acidic protons with diazobenzilidene-functionalized glass slides,[179] and a photoaffinity reaction.[180] Many research groups have employed a two-step approach, where the amine-functionalized SAM was derivatized with a linker molecule after self-assembly to increase the reactivity of the monolayer. Heterobifunctional reagents such as *N*-succinimidyl-6-maleimidocaproate react with APS monolayers to expose the maleimide functionality, which in turn can be used in a Michael addition with sulfanyl groups.[181–183] A critical feature of this methodology is the resistance to nonspecific adsorption, which was attributed to the hydrophilicity of the maleimide functionality.[183] It has also been shown that the same heterobifunctional molecule could be attached to a sulfanyl-terminated SAM.[184] In this case it was utilized to link an amine-containing, fluorescently labeled oligodeoxynucleotide probe to the surface for hybridization experiments. A slightly different approach to attach DNA covalently to glass surfaces was reported by O'Donnel et al.[185] They applied a heterobifunctional cross-linking agent to incorporate an iodoacetamido group, which was treated with a reduced oligodeoxynucleotide presenting free sulfanyl groups.

As was mentioned before, resistance to nonspecific adsorption is a critical issue when designing microarrays. Sekal et al. described a method to prepare monolayers that are resistant to nonspecific protein adsorption and present primary amino groups for derivatization.[186] By treating an APS layer with glutaraldehyde and subsequently with 2,2′-(ethylenedioxy)bis(ethylenediamine) they were able to incorporate ligands and protein-sensitive fluorescent reporter groups, and used these monolayers for the detection of protein–ligand interactions.

Efficient surface silylation reactions can be complicated by formation of inhomogeneous layers, poor surface coverage, and instability to frequent regeneration steps.[187] To overcome these problems, Benters et al. developed a method for generating highly homogeneous activated silicon oxide surfaces that can be applied to the efficient coupling of oligonucleotides to produce DNA microarrays.[187] The method involves the initial formation of an APS layer, which is activated by a homobifunctional linker such as 1,4-phenylenediisothiocyanate (DITC), and then allowed to react with a starburst dendrimer containing 64 primary amino groups at the periphery. The attached dendritic molecules are subsequently activated and cross-linked with a homobifunctional spacer to display a surface with high coverage and decreased steric hindrance, and that is resistant against repeated regeneration procedures. Recently, layers obtained by this procedure and APS layers were derivatized with appropriate phosphane groups to immobilize azido-functionalized biomolecules by Staudinger ligation.[188,189] This coupling strategy affords rapid immobilization and offers the advantage that it is compatible with unprotected functional groups, which are often required for interactions in biological systems.

Epoxy-terminated SAMs can react with molecules bearing amino groups. In this way it was possible to bind cyclopeptides to the glass surface for use as a molecular receptor[190] and to determine binding constants between an immobilized tripeptide and vancomycin using confocal fluorescence detection.[191] Hydrolysis of an epoxide-functionalized SAM yields a diol-functionalized SAM, which was used to develop a biosensor of immobilized nucleic acid aptamers to detect nonlabeled targets such as proteins.[192]

Another relatively simple coupling strategy involves the reaction of aldehyde-modified glass surfaces with amine-containing molecules. The aldehydes react readily with primary amines of proteins or DNA to form a Schiff base linkage.[177,193] This strategy was applied to prepare libraries of peptidyl coumarins in microarrays. It was demonstrated that the immobilized peptides were accessible for proteolytic cleavage.[194]

Other reported strategies to attach biological molecules to SiO_2 surfaces involve the reactions of sulfanyl-terminated SAMs with disulfide-modified oligonucleotides or heme proteins,[195,196] iodopropyl monolayers with sulfanyl-containing proteins,[197] alcohols with a silyl chloride surface,[198] and bromoacetamide SAMs with phosphorothioate-functionalized oligonucleotides.[199]

4. Engineering the Silicon Oxide Surface Using Self-Assembled Monolayers

The development of methods to control surface chemistry on the 1–100-nm length scale is a fundamental challenge in nanoscience and nanotechnology because it opens up new possibilities in fields ranging from molecular electronics to biomedicine and catalysis.[200] SAMs offer an ideal platform for engineering surfaces on a molecular level, provided that techniques are developed to pattern or assemble SAMs with high resolution and fidelity.

4.1. Spacing of Chemical Functionalities

The positioning of chemical groups at regular intervals on a surface is of technological importance to localize adsorption and tune surface coverage, for example. The density of probe molecules is a critical issue in the design of DNA and protein chips. A facile method to achieve low surface coverage of functional groups is by preparing multicomponent SAMs so that chemical functionalities are diluted in an "inert" matrix of other molecules, which might be either unfunctionalized or carry a different functionality. Several approaches have been described in the literature, of which the most widely used involves competitive chemisorption, that is, the treatment of a surface with a mixture of adsorbates. Although the composition and properties of mixed monolayers are not at all straightforward, numerous binary monolayers have been prepared, as listed by Fadeev and McCarthy in Ref. [201].

Fan et al. stimulated phase separation in a binary monolayer by using two very different alkylsilane amphiphiles—one with strong cohesive interactions and one able to form hydrogen bonds—to generate a surface with nano-islands of a chemical functionality.[202] The surface composition was analyzed by AFM, which showed pronounced differences in height and friction for the two components. The phase behavior of multicomponent SAMs could be used as an effective "latent image" to generate features on the surface by wet etching.[203] This difference in etch resistence was achieved by the assembly of molecules with different chain length, and it was proposed that regions of more densely packed molecules were more etch resistant than regions of less coherent packing. Mixed SAMs can be conveniently used to control the surface free energy, as was shown in an elegant experiment by Lee et al.[204] They used different ratios of hydroxy and methyl groups to tailor the surface free energy of silicon substrates, and found that in this way they could control the growth modes of atomic layer deposition (ALD) of TiO_2.

An alternative approach for the preparation of "mixed surfaces" involves reaction of partially silanized surfaces with a second silane. As mentioned earlier, SAMs on SiO_2 grow through an island growth mechanism, thus offering the possibility to fill partial monolayers of one component with another. Recent examples have reported small domains of OTS islands filled with bromine-terminated[205] and amino-terminated SAMs.[206] Fadeev and McCarthy have used a very bulky silane for deposition, and found by size-exclusion contact angle hysteresis measurements that nanopores with a cross-section of about 0.5 nm^2 were still present at the surface, and accessible to probes of smaller dimension.[201] In this way uniformly mixed binary monolayers were generated (Figure 5).

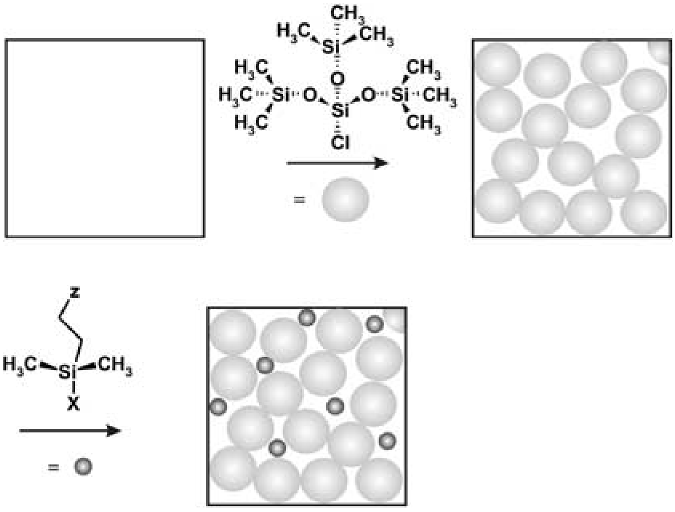


Figure 5. Schematic representation of a two-step silanization procedure.[201]

A different strategy to achieve the positioning of chemical functionalities on a surface comprises the self-assembly of large molecules carrying only one type of functional group. Focally functionalized dendrons appear to be particularly suitable molecules for this method (Figure 6). Sub-monolayers, monolayers, and multilayers of trichlorosilane-terminated carbosilane dendrons with a phenyl group at the focal point were reported by Cai and co-workers.[207,208] Dendrons bearing carboxy groups at the periphery and a protected amine at the focal point were assembled on an amino-terminated SAM through multiple ionic interactions.[209] AFM and fluorescence measurements indicated the formation of a close-packed layer with spacings between the amino functional groups of 24–34 Å.

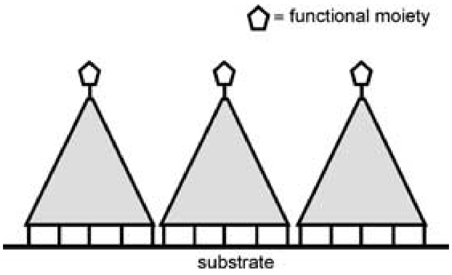


Figure 6. Schematic illustration of the concept of using large molecules to control the spacing between functional groups at a surface.

SiO_2 surfaces with spacially separated functionalities are relatively easily prepared by the methods described above, without the use of expensive machinery. The process is flexible, useful on a large scale, and not restricted to flat surfaces. However, a significant drawback of these approaches is that only homogeneous surfaces can be generated and the functionalities cannot be positioned or patterned accurately, as is required for the bottom-up construction of nanosized functional entities.

4.2. Patterning Self-Assembled Monolayers with Photons and Particles

4.2.1. Photolithography

Photolithography on SAMs relies on the absorption of radiation in the exposed regions of the monolayer which undergo photocleavage to yield surface residues. The use of less expensive equipment, compared to, for example, electron beam lithography (see Section 4.2.2), makes this a popular method to create patterned SAMs, but the feature sizes that can be achieved are diffraction-limited.

Irradiation with light in the deep UV region has been used extensively to remove SAMs in exposed regions. This leaves an activated surface that can be used for numerous post-patterning processes. SAMs of different chemical functionalities were deposited for the immobilization of fluorophores,[210] for cell adhesion,[211] and to control the surface potential.[212,213] The remaining SAMs have been used as a mask for wet chemical etching to fabricate microstructures on Si substrates[214,215] and as a template for Pd adhesion and subsequent electroless deposition of ZnO.[216] The exposed areas could be used as templates for electroless plating of Ni,[210,215] and for the deposition of TiO_2 films.[217] Recently, photocatalytic lithography of alkylsilane SAMs was reported using UV light and TiO_2 to rapidly and homogeneously remove the SAM by the generation of highly reactive oxygen species.[218]

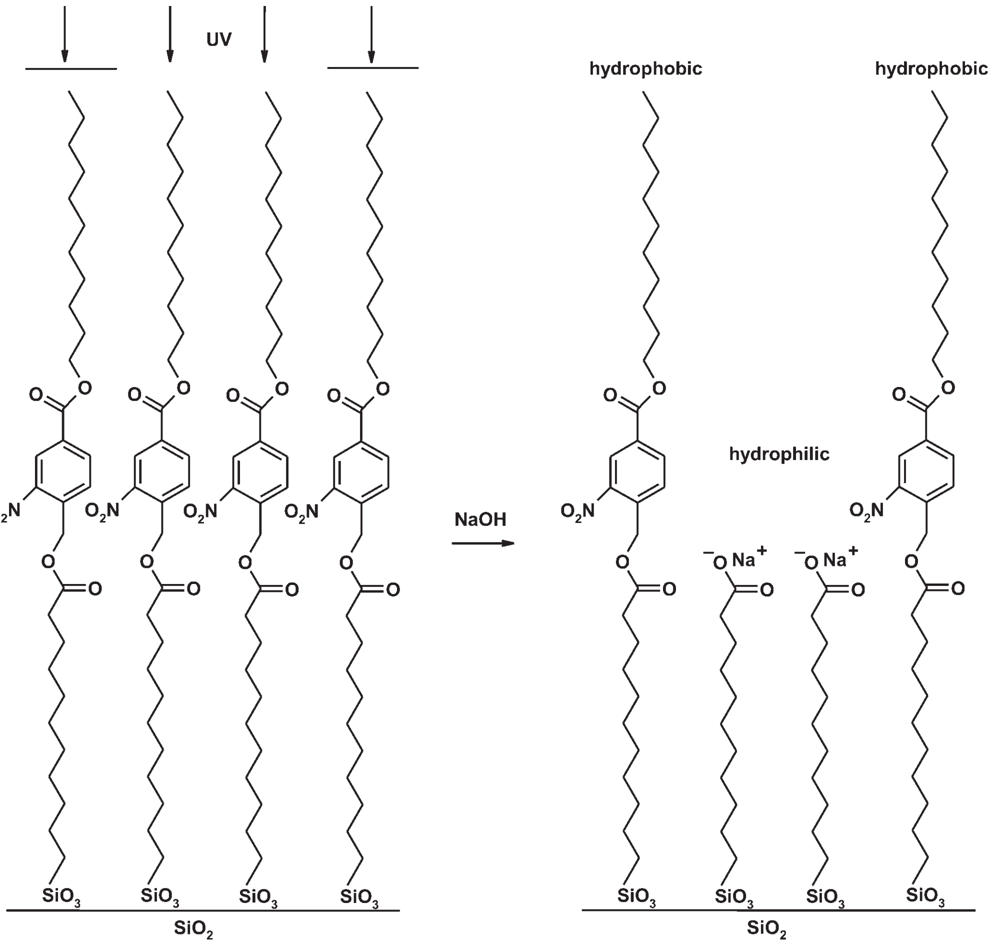
Instead of completely removing the monolayer, photolithography can also be used to create patterns with different chemical functionalities. Some research groups have reported photodeprotection of protected amino groups, after which the exposed areas could be selectively developed by the adsorption of fluorescent particles.[219,220] A very elegant example is the combination of photolithography with the immobilization of biomolecules for the generation of, for example, DNA chips.[221] Pioneering work in this field was conducted by Fodor and others.[222–225] They used light-directed, spatially addressable parallel synthesis to build arrays for rapid DNA analysis. The pattern of illumination through a mask, using light to remove photolabile protecting groups from selected areas, determines which regions of the surface are activated for coupling. The first set of building blocks, each bearing a photolabile group, is exposed to the surface but reacts only with the patterned areas. The substrate is subsequently illuminated through another mask for deprotection and coupling with a second building block. The steps of masking/irradiation and coupling are repeated to introduce various oligomers. The patterns of the masks and the sequence of reagents define the ultimate sequences synthesized, and their locations on the surface are known.

Other chemical transformations have been shown by the research groups of Dressick and Sugimura. Dressick and co-workers were able to transform 4-(chloromethyl)phenyl chromophores into phenylaldehyde groups, which in turn could be reduced to amines.[226] Sigimura et al. showed that OTS SAMs decomposed gradually upon exposure to UV light in a vacuum to generate carboxilic acid groups that were successfully treated with functionalized and fluorinated silanes.[214,215] Surface wettability could also be controlled using photolithographic methods. In a series of publications Beebe and co-workers reported cunning experiments to control liquid flow inside microchannels.[227–229] Surface free energies were patterned by use of SAMs in combination with photolithography (Scheme 3). They could confine the flow of aqueous liquids to the hydrophilic pathways, provided that the pressure was maintained below a critical value.

Photolithography has recently been applied in a constructive procedure.[230] Direct writing with a laser allowed the formation of sub-200 nm oxide patterns on H-terminated Si. Exposing these substrates to a solution containing OTS molecules resulted in selective growth on the oxide patterns.

4.2.2. Electron Beam Lithography

SAMs are candidates for very high resolution resists in electron beam lithography. Since the feature size generated with electron beam lithography depends on the thickness of the resist, the monomolecular thickness of SAMs could reduce back scattering of electrons and provide ultrahigh-resolution electron beam patterning. It has been shown that patterns of several tens of nanometers could be created in OTS and perfluorinated SAMs on SiO_2, and that the patterns could be transferred into the substrate by wet-etching techniques.[231–233] Patterns smaller than 10 nm could also be attained by using scanning electron microscopy (SEM) with a small beam diameter.[234] A different development of the created patterns was reported by Marrian et al.[235] Low voltage electron beam lithography was used to pattern films and the patterns were applied as templates for the electroless

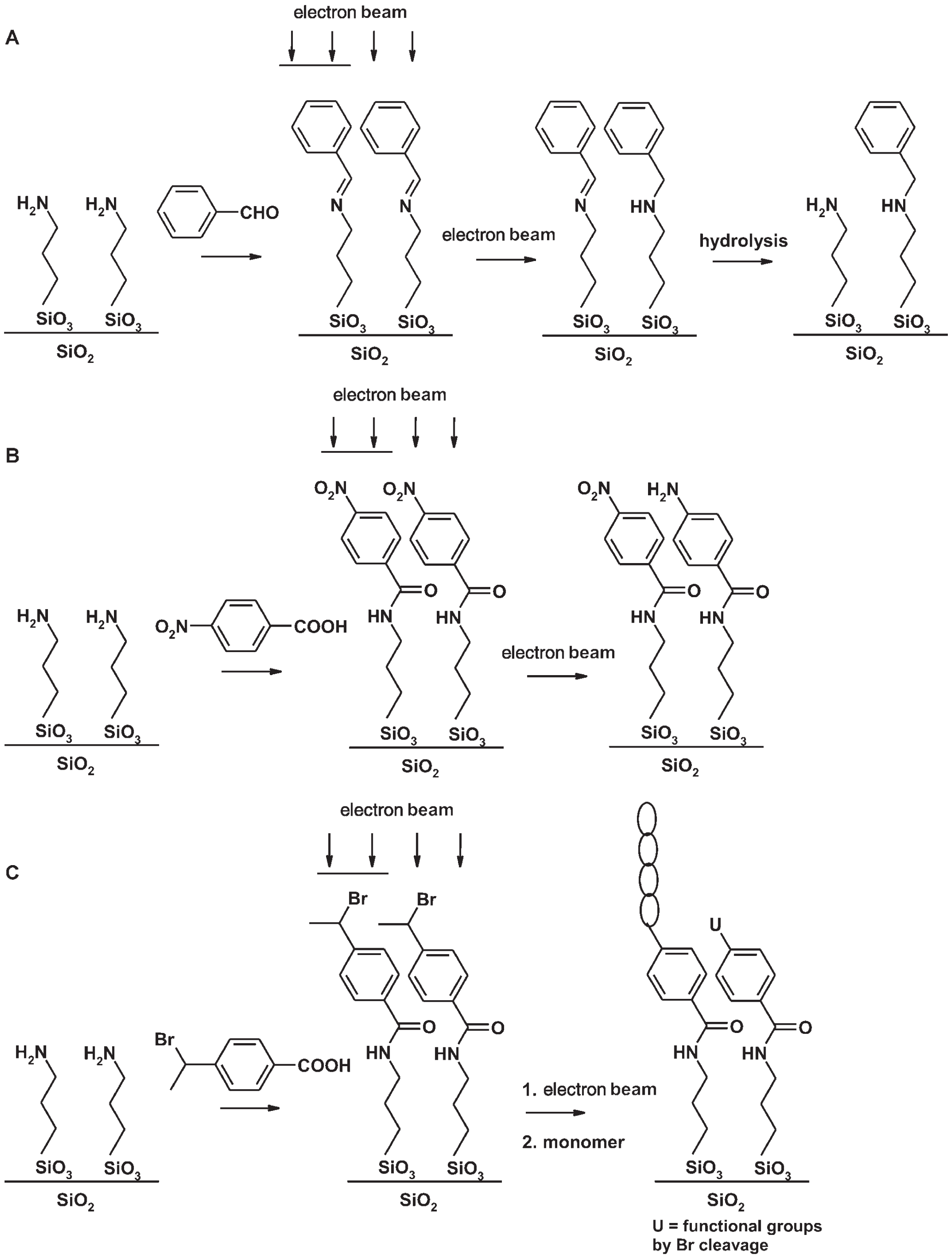


Scheme 3. UV photolithography to fabricate hydrophilic patterns inside microchannels.[227]

plating of thin Ni films. Linewidths down to about 20 nm were observed after plating.

There have been several reports that combine electron beam lithography with functionalized SAMs. Craighead and co-workers patterned amino-terminated SAMs and developed the patterns by exposing them to palladium colloids and coated polystyrene fluorescent spheres.[236] The colloids and spheres adhered only to unexposed areas of the monolayers. Other studies employed the deposition of aminosilanes through a poly(methylmethacrylate) (PMMA) mask or an unfunctionalized SAM that was patterned by electron beam lithography.[237–239] In this way colloidal particles and carbon nanotubes were deposited selectively on the amine-modified parts of the substrate.

Recently, electron beam irradiation was used to induce chemical transformations in monolayers. Park and co-workers studied several procedures to prepare patterned amino- and bromo-terminated SAMs, and verified the reactivity by attaching biotin/streptavidin groups,[240] or amplified the patterns vertically by radical polymerization.[241] The transformations are shown in Scheme 4. The induced transformations have been employed to direct adsorption of gold nanoparticles.[242] In addition, sub-50 nm patterns were prepared in SAMs with embedded disulfide bonds.[243] Phenyl-3-



Scheme 4. Chemical transformations of SAMs with a low-energy electron beam.[240,241]

(trimethoxysilylpropyl)disulfide monolayers were patterned with electron beam lithography, which generated 3–4-Å deep and 30-nm wide trenches. XPS indicated the cleavage of the disulfide bonds to sulfhydryl groups, and the resulting chemical patterns could be developed by reaction with *N*-(1-pyrene)maleimide. Even smaller chemical patterns were obtained by a combination of electron beam lithography and gas-phase silanization.[244] It was shown that monolayers with varying chemical functionalities could be formed through nanoholes in a PMMA mask. After removing the mask, a monolayer of different functionality was deposited, and generated well-defined nano-islands as small as 20 nm of one chemical functionality in a matrix of another.

4.2.3. Ion-beam and X-ray Lithography

Ion-beam and X-ray lithography are methods that have been less frequently used to pattern SAMs on SiO_2. Patterning with low-energy ion beams usually employs shadow masks because of the difficulty of focusing such sources. However, high-energy focused ion beams (FIBs) should result in nanometer-scale patterns, as it is possible to attain beam diameters as small as 8 nm.[245] FIBs have already been used to write 10-nm wide features in thin PMMA films.[246] A vinyl-terminated monolayer was selectively deposited in ion-beam-etched regions of a methyl-terminated SAM with a resolution of 1–3 μm.[247] Ada et al. have studied in detail the interaction of low-energy ions with organosilane SAMs, and were able to create 300-nm wide gaps by employing FIB.[248] Smaller feature sizes were reported by exposing monolayers to low doses of slow, highly charged ions, such as Xe^{41+} and Th^{73+}.[249] AFM images showed craters from single ion impacts with diameters of 50–63 nm. Equally small features have also been reported by Whitesides and co-workers by utilizing a beam of neutral Cs atoms.[250]

Irradiation with soft X-rays through a mask can be a convenient method for chemical patterning of monolayers. Reported transformations include the loss of halogens in halogenmethylphenylsilyl layers,[251,252] and the cleavage of nitro groups in nitro-substituted aromatic SAMs.[253] La et al. used masks with nanometer-sized features to develop sub-100 nm patterns, as evidenced by AFM.[254] The patterns could be derivatized by attachment of fluorescently labeled oligonucleotides. Irradiation of OTS layers resulted in the formation of oxygen-containing groups such as OH and C(O)H.[255] Pattern transfer of features with dimensions as small as 150 nm into the underlying substrate were obtained by reactive ion etching using thin films of Ni selectively deposited onto the exposed areas of the OTS SAM.

Recently, it was shown that hybrid patterning strategies allow for the fabrication of defect-free nanopatterns of block copolymers.[256] A photoresist on top of a phenylethyl monolayer was patterned with 45–55-nm-sized features by interferometric lithography using extreme UV light, and the pattern was transferred into the underlying SAM by chemical modification using soft X-rays. After removing the photoresist, poly(styrene-*block*-methylmethacrylate) (PS-*b*-PMMA) was spin-coated onto the patterned SAM and annealed. It was found that the PMMA block preferentially wetted the modified regions of the surface, and thus domain structures were formed analogous to the SAM patterns, as observed by SEM (Figure 7).

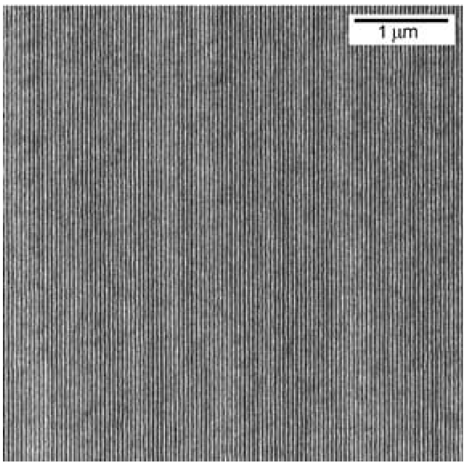


Figure 7. SEM image of 48-nm wide PS and PMMA domains formed by selective absorption on a SAM patterned by a combination of UV and X-ray lithography.[256]

4.3. Soft Lithography

Soft lithography[257] is the collective name for a set of lithographic methods including replica molding, microcontact printing (μCP), and micromolding using a patterned elastomer as a mold, stamp, or mask to transfer a pattern.[258] Soft lithography offers advantages over other lithographic methods for the patterning of nonplanar substrates, unusual materials, or large areas.[258] Of these techniques, μCP has been employed most frequently for the facile (sub)micron patterning of surfaces. μCP relies on the inking of an elastomeric (usually PDMS) stamp with suitable molecules. When the stamp is brought into contact with a substrate, the molecules are transferred from the stamp to the substrate in the regions of contact. μCP was initially developed for the patterning of gold surfaces with alkanethiols, and even today the bulk of the literature comprises patterning of this surface with these adorbates.

Reports regarding μCP on SiO_2 surfaces have been rather limited. This situation might be explained by the inherent sensitivity of trialkoxy- and especially trichlorosilanes, and the lower edge resolution of silanes on SiO_2 relative to thiols on gold.[259] Although Whitesides and co-workers reported that printed OTS SAMs were only partly etch resistant, later studies showed that printed patterns could be transferred into the underlying silicon substrate,[260] even with feature sizes as small as 80 nm.[261] Detailed studies by Nuzzo and co-workers indicated that close-packed OTS monolayers were formed after only 30 s of printing while it took minutes to form a densely packed monolayer by deposition from solution.[262] They also found that stable SAMs were formed, but that patterning at dimensions less than a few micrometers resulted in the spreading of OTS in regions that had not been in contact with the stamp. μCP with docosyltrichlorosilane resulted in more accurate transfer to the substrate, and these films had an improved etch-resistance.[263]

Amplification of a printed pattern can also be achieved in a different manner. Harada et al. amplified a printed vinyl-terminated pattern by selectively attaching a Ru complex, which reacted with norborene derivatives to give thin polymer films.[264] The contrast in wettability between clean SiO_2 and a printed OTS pattern enabled the confinement and alignment of molecules.[265] After printing, the remaining hydrophilic parts of the substrate were covered with a thin polyelectrolyte layer, onto which biological macromolecules and liquid crystals could be confined. This process afforded a straightforward way to create microchannels on a surface.

The majority of the work concerning μCP of SAMs on SiO_2 involves deposition of metals. Printed monolayers can serve as a resist for chemical vapor deposition of copper,[266] or deposition of $SnCl_2$ from solution, which serves as a nucleation point for electroless plating of Ag.[267]

Instead of printing a monolayer, it is also possible to print onto a monolayer assembled from solution. Hidber et al. used an amino-terminated SAM as an adhesion promoter to print (sub)micron patterns of Pd colloids.[268] The immobilized colloids served as a catalyst for the electroless deposition of copper, and yielded (sub)micrometer-scale copper lines on an insulating surface. Recently, Reinhoudt and co-workers introduced supramolecular μCP, which is shown schematically in Figure 8.[269–271] In this method, guest molecules that bind through multiple supramolecular interactions were printed onto a densely packed monolayer of cyclodextrin receptor molecules on SiO_2 (or gold). The patterns were characterized by AFM, XPS, and confocal microscopy. Control experiments showed that the ink molecules bind to the receptor surface through specific host–guest interactions. One advantage of this method is that the stability of the assemblies can be tuned by the number of interactions between the guest molecules and host monolayer.

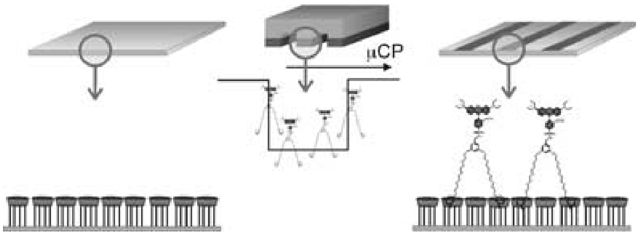


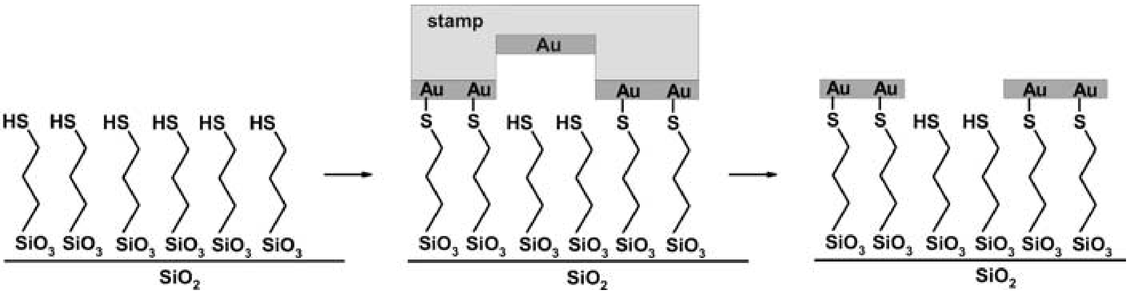
Figure 8. Schematic representation of supramolecular microcontact printing (μCP). Cyclodextrin host monolayers are patterned by μCP of suitable guest molecules.[269,270]

Sulfanyl-terminated MPTMS SAMs can be employed as adhesion promoters for noble metals.[272] In nanotransfer lithography a gold-coated PDMS stamp is used to transfer thin but stable gold layers onto the monolayer (Scheme 5). In a series of publications Delamarche et al. described an elegant process to produce NiB stuctures and metal nanowires on glass substrates.[273–277] They combined the adhesive properties of an amino-terminated SAM to bind Pd/Sn colloids, which were used to initiate electroless deposition of NiB. Then, copper was electroplated and patterned by μCP using a protective layer of thiol molecules. The pattern was subsequently etched into the copper and NiB by two wet etching techniques. This process was developed to provide a new and potentially cost-effective way for the fabrication of gate layers in thin-film transistor (TFT) LCDs, and could even be applied on a macro (38 cm) scale.

Nanoimprint lithography (NIL)[278] was recently advocated as a powerful alternative to μCP of organosilanes.[279] A PMMA polymer template obtained by NIL directs the assembly of a SAM from the gas phase to the uncovered area of the substrate while preventing the formation of a SAM in the covered area. After removal of the polymer, SAM patterns are obtained that may be filled with other silanes. NIL-patterned SAMs are useful in nanofabrication, for example, to direct adsorption of particles or deposition of metal electrodes on SAMs (Figure 9).

4.4. Scanning Probe Lithography

Scanning probe microscopy can visualize surface topography and surface chemistry at the submolecular level. In addition, probe tips can be used to manipulate atoms and molecules on surfaces, and in this mode the technique is often referred to as scanning probe lithography.[280] Sugimura et al. were among the first to combine a scanning probe tip with self-assembly on SiO_2 surfaces to create nanoscale patterns. They have used a scanning tunneling microscope tip for local anodization of a Si-H surface to SiO_2 in the presence of an organosilane vapor.[281] This resulted in the formation of monolayer features of 20 nm that showed a resistance to chemical etching. Other studies from the same authors reported patterning of a homogeneous monolayer by apply-



Scheme 5. Metal structures prepared on adhesive SAMs by nanotransfer printing.[272]

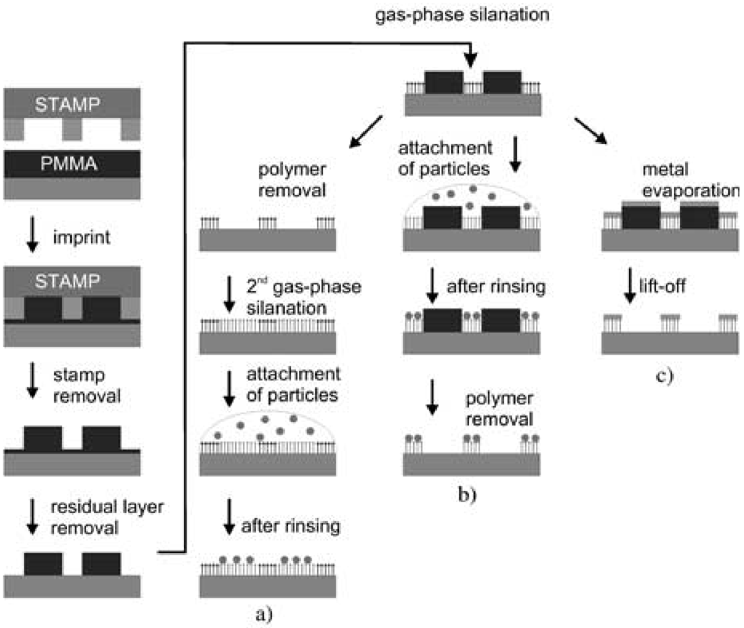


Figure 9. Nanofabrication using SAMs patterned by nanoimprint lithography. Applications: a) Polymer removal, evaporation of a second silane, and selective attachment of functionalized particles. b) Selective attachment of functionalized particles, and polymer removal. c) Metal evaporation and metal lift-off.[279]

ing a bias voltage to the probe tip, effectively removing the monolayer from the probe-scanned regions. Next, the exposed regions were filled with SAMs of different chemical composition to regulate the surface potential or selectively assemble proteins at a spatial resolution on the nanometer scale.[282,283] A different method for nanometer-scale patterning was obtained by field-induced oxidation (FIO) using a conductive cantilever.[284] Surface hydroxy groups, necessary for monolayer formation, were removed and monolayer formation was suppressed when FIO was employed locally on an oxide surface in a dry nitrogen atmosphere. In this way, a line structure of an OTS SAM as narrow as 22 nm could be fabricated. In contrast, OTS SAMs formed on the entire surface when FIO was performed under humid conditions.

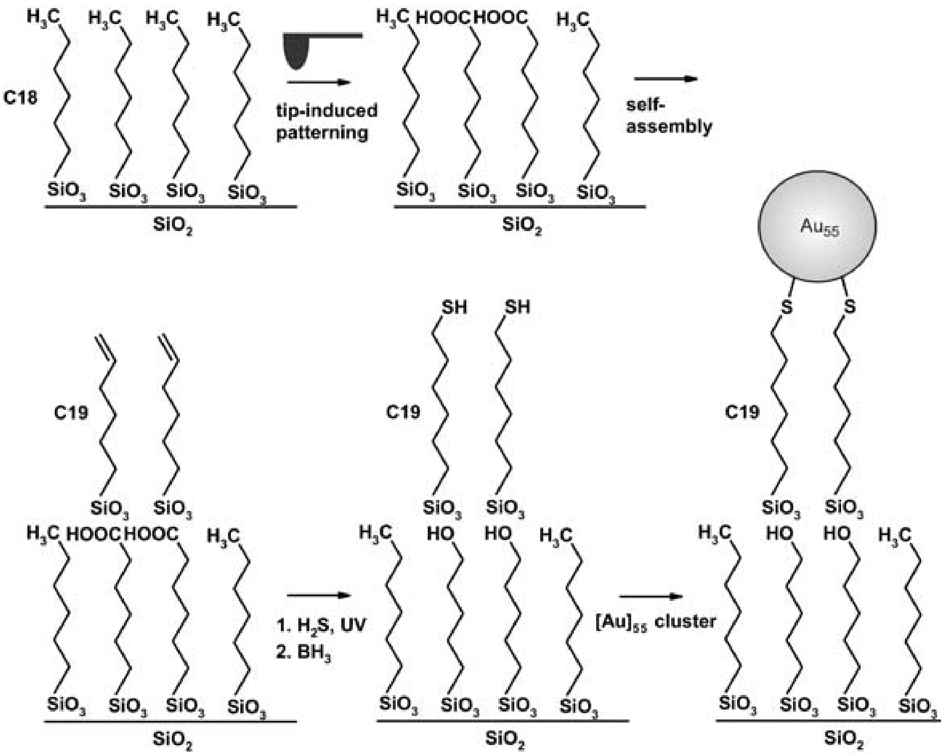
4.4.1. Constructive-Nanolithography

Constructive nanolithography was introduced by Sagiv and co-workers.[285] It involves nondestructive surface patterning by means of an electrical bias to a conducting AFM tip operated under ambient conditions, followed by template-controlled self-assembly. The versatility of this approach was demonstrated in several systems where vinyl-terminated and OTS SAMs were locally electrooxidized to prepare patterned bilayers,[286] self-assembled metal islands,[285,287] metal nanoparticles,[288–290] and nanowires.[289] Features with sub-50 nm dimensions could be fabricated by using this method. A schematic representation of the organosilane template pattern and the self-assembly of $[Au_{55}]$ clusters on the template is displayed in Scheme 6. This methodology could be used for the nanometer to millimeter range by employing electrooxidation with a rigid metallic stamp.[291] Recently, other research groups have applied local probe oxidation of SAMs for functionalization with cationic gold nanoparticles, quaternary ammonium salts, and polymers.[292,293]

A few years before Sagiv and co-workers introduced constructive nanolithography, a similar approach was presented by Schultz and co-workers, who made use of a catalytic probe.[294] In this elegant experiment an alkylazide monolayer was reduced to its corresponding amine by a catalytic Pt coated AFM tip. The amino groups were then covalently modified with fluorescently labeled beads and imaged under a confocal microscope.

4.4.2. Dip-Pen Nanolithography

Dip-pen nanolithography (DPN)[200,295] uses an inked AFM tip to deposit molecules on a substrate. This technique, which is believed to rely on the transport of molecules from



Scheme 6. Schematic representation of constructive nanolithography, in which tip-induced electrooxidation and subsequent self-assembly on the written template are employed. In this case $[Au_{55}]$ clusters were assembled.[288]

the tip to a surface through a water meniscus, has been used to generate structures with line widths as small as about 10 nm (Figure 10a). Reported examples have dealt almost exclusively with the writing of thiol inks on gold substrates, or the use of metal salts for the electrostatical assembly on appropriately biased silicon substrates.

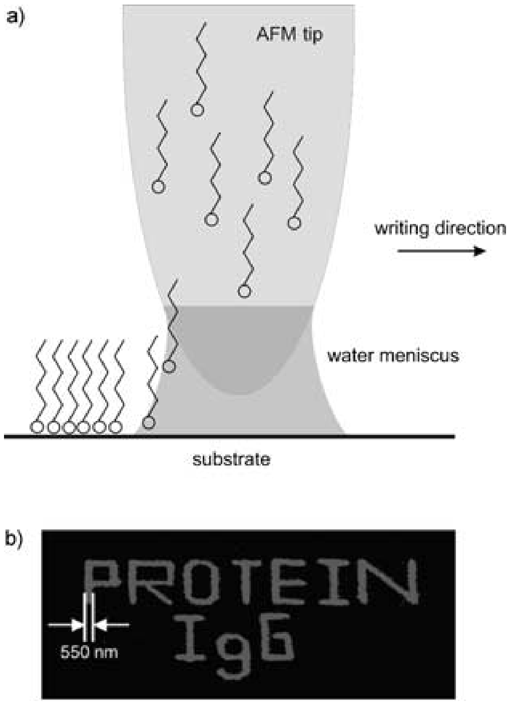


Figure 10. a) Schematic representation of dip-pen lithography (DPN). b) Fluorescence image of DPN-generated labeled antirabbit IgG structure on SiO_2.[301]

Thus far, silane-based inks have rarely been used, mainly because of the incompatibility of chloro- and alkoxysilane groups with the water meniscus that mediates ink transport. Ivanisevic and Mirkin used hexamethyldisilazane to write organic patterns on SiO_2 with sub-100 nm dimensions.[296] Two recent articles, however, demonstrated that it is possible to write with trialkoxysilane-based inks. Pena et al. wrote APS and MPTMS lines of nanometer dimensions, but were not able to further derivatize the formed structures.[297] They explained this lack of reactivity by the formation of multilayers through hydrogen bonding. These results were contradicted in a study by Jung et al.,[298] who claimed that DPN with reactive silanes is possible if proper measures against polymerization are taken. Writing at low humidity resulted in the formation of 110-nm-wide MPTMS lines, which were successfully treated with biotin and fluorescently labeled streptavidin.

An alternative method to write functionalized structures on the SiO_2 surface constitutes writing on functional monolayers. Reinhoudt and co-workers recently demonstrated supramolecular DPN where an AFM tip is inked with suitable guest molecules and the substrate is a β-cyclodextrin host monolayer.[270] Sub-500 nm patterns, based on host–guest interactions, were written and imaged by confocal microscopy and AFM. Covalently anchored nanoscale patterns of oligonucleotides and maleimide-linked biotin were written onto MPTMS SAMs.[299,300] It was found that nanoscale patterning of maleimide-linked biotin was facilitated by the addition of small amounts of non-ionic surfactant to the biotin ink. An increase in the wettability of the substrate is thought to cause this phenomenon.

The direct writing of proteins on modified SiO_2 surfaces has been reported.[301] A negatively charged surface was used to bind proteins electrostatically (Figure 10b), and proteins were covalently bound by writing on a preformed aldehyde-terminated monolayer. Some modifications to the writing process had to be made. First, an AFM tip coated with poly(ethylene glycol) (PEG) was used to minimize protein adsorption and to reduce the activation energy required for protein transport from the tip to the surface. In addition, it protects the protein from denaturation on the tip surface. Second, it was found that high humidity is a prerequisite for writing with high-molecular-weight molecules. Patterning was performed at relative humidities between 60 and 90%, whereas low humidities were sufficient for writing with low-molecular-weight trialkoxysilanes.

5. Summary and Outlook

Since the first report on SAMs on SiO_2 in 1980, many studies have investigated the mechanism of monolayer formation, which has led to a better understanding of the principles underlying this self-assembly process. It has become clear that factors such as solvent, temperature, water content, deposition time, and age of the adsorbate solution play a crucial role in the self-assembly process. Small variation of one or more of these factors can result in very different assembly properties, and several studies appear to have conflicting outcomes. An illustrative example is the temperature at which the self-assembly takes place: Lower temperatures favor island growth, while at higher temperature homogeneous growth has been observed. In addition, several studies have shown that the assembly process is not so much covalent in nature as had been assumed for a long time. Adsorbate molecules that covalently attach to the surface are scarce, and in-plane polymerization of the adsorbates might lead to decreased order instead of a close-packed monolayer. These results indicate that the monolayers have Langmuir-like features, as was elegantly demonstrated by reversible temperature-dependent island-growth formation of sub-monolayers.[67]

Chemical derivatization of SAMs on SiO_2 is essential for many potential applications. Two factors determine the versatility of functional SAMs on SiO_2: the range of functionalities that are tolerated in the self-assembly of stable and ordered SAMs, and the scope of chemical post-modifications that can be achieved. Not all functional groups can be conveniently introduced in the self-assembly process because of the inherent reactivity of the trichloro- or trialkoxysilanes that are used for chemisorption. In addition, functional groups might interact with the polar surface, thus resulting in the formation of disordered monolayers. For these reasons chemical postmodifications have been studied in depth and a wide range of surface chemistry is nowadays available for further derivatization of the SAMs. Selective attachment of compounds to the surface under mild conditions, while avoiding nonspecific interactions, is crucial particularly for the development of bioanalytical surfaces. These reactions should be compatible with a wide variety of functional groups that occur in biologically relevant molecules. Bifunctional coupling agents are often used to meet these requirements.

Positional control of surface chemistry on the nanoscale allows the development of arrays containing a high density of chemical information. The chemical information can then be translated into high-density functional surfaces, such as proteins or DNA chips, or be exploited as a platform for building nanosized functional materials (for example, by self-assembly). The ability to pattern surfaces with chemical information is therefore of prime importance. Electron beam lithography, and especially photolithography, have been the principal techniques for the patterning of surfaces for many years, but soft and probe lithographic techniques have recently witnessed a tremendous development. The main advantages of these methods include the use of inexpensive equipment, the high (sub-100 nm) resolution, and the possibility to prepare positive patterns under mild conditions.

The logical extension of surface patterning is to express and amplify a 2D pattern into a 3D structure. This is a requirement for the bottom-up fabrication of nanoscale devices. Taking nature as a source of inspiration, it is expected that self-assembly techniques will play a major role in nanofabrication. Striking examples of this trend have already been published by Sagiv and co-workers, who used self-assembly techniques to translate a chemical pattern into nanostructures of colloidal gold,[288] and by Mirkin and co-workers, who employed an AFM tip to write protein structures on a SAM.[301] It is expected that this trend from 2D to 3D will be continued in the next decade, while the focus of research in this area will shift more and more toward the nanofabrication of devices.

The authors are grateful to Jacob Sagiv for helpful suggestions. The Microchemical Systems (MiCS) program of the MESA$^+$ Institute for Nanotechnology is acknowledged for financial support.

Received: February 21, 2005

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[1] *New Scientist* **1983**, *98*, 20.
[2] L. Netzer, J. Sagiv, *J. Am. Chem. Soc.* **1983**, *105*, 674.
[3] W. C. Bigelow, D. L. Pickett, W. A. Zisman, *J. Colloid Sci.* **1946**, *1*, 513.
[4] W. C. Bigelow, E. Glass, W. A. Zisman, *J. Colloid Sci.* **1947**, *2*, 563.
[5] E. E. Polymeropoulos, J. Sagiv, *J. Chem. Phys.* **1978**, *69*, 1836.
[6] J. Sagiv, *J. Am. Chem. Soc.* **1980**, *102*, 92.
[7] A. Ulman, *An Introduction to Ultrathin Organic Films*, Academic Press, Boston, **1991**.
[8] A. Ulman, *Chem. Rev.* **1996**, *96*, 1533.
[9] D. K. Schwartz, *Annu. Rev. Phys. Chem.* **2001**, *52*, 107.
[10] J. C. Love, L. A. Estroff, J. K. Kriebel, R. G. Nuzzo, G. M. Whitesides, *Chem. Rev.* **2005**, *105*, 1103.
[11] R. G. Nuzzo, D. Allara, *J. Am. Chem. Soc.* **1983**, *105*, 4481.
[12] L. Netzer, R. Iscovici, J. Sagiv, *Thin Solid Films* **1983**, *99*, 235.
[13] L. Netzer, R. Iscovici, J. Sagiv, *Thin Solid Films* **1983**, *100*, 67.
[14] R. Maoz, J. Sagiv, *J. Colloid Interface Sci.* **1984**, *100*, 465.
[15] J. Gun, R. Iscovici, J. Sagiv, *J. Colloid Interface Sci.* **1984**, *101*, 201.
[16] J. Gun, J. Sagiv, *J. Colloid Interface Sci.* **1986**, *112*, 457.
[17] S. R. Cohen, R. Naaman, J. Sagiv, *J. Phys. Chem.* **1986**, *90*, 3054.
[18] R. Maoz, J. Sagiv, *Langmuir* **1987**, *3*, 1034.
[19] R. Maoz, J. Sagiv, *Langmuir* **1987**, *3*, 1045.
[20] H. Brunner, M. Vallant, U. Mayer, H. Hoffmann, *J. Colloid Interface Sci.* **1999**, *212*, 545.
[21] V. I. Nefodov, *X-ray Photoelectron Spectroscopy of Solid Surfaces*, VSP, Utrecht, **1988**.
[22] J. C. Vickerman, *Surface Analysis—The Principal Techniques*, Wiley, Chichester, **1997**.
[23] B. Hagenhoff, A. Benninghoven, K. Stoppeklangner, J. Grobe, *Adv. Mater.* **1994**, *6*, 142.
[24] D. L. Angst, G. W. Simmons, *Langmuir* **1991**, *7*, 2236.
[25] S. Flink, F. C. J. M. van Veggel, D. N. Reinhoudt, *Adv. Mater.* **2000**, *12*, 1315.
[26] S. R. Wasserman, G. M. Whitesides, I. M. Tidswell, B. M. Ocko, P. S. Pershan, J. D. Axe, *J. Am. Chem. Soc.* **1989**, *111*, 5852.
[27] S. N. Magonov, M.-H. Whangbo, *Surface Analysis with STM and AFM*, VCH, Weinheim, **1996**.
[28] L. T. Zhuravlev, *Langmuir* **1987**, *3*, 316.
[29] H. O. Finklea, L. R. Robinson, A. Blackburn, B. Richter, D. Allara, T. Bright, *Langmuir* **1986**, *2*, 239.
[30] D. L. Allara, A. N. Parikh, F. Rondelez, *Langmuir* **1995**, *11*, 2357.
[31] P. Silberzan, L. Leger, D. Ausserre, J. J. Benattar, *Langmuir* **1991**, *7*, 1647.
[32] C. P. Tripp, M. L. Hair, *Langmuir* **1992**, *8*, 1120.
[33] C. P. Tripp, M. L. Hair, *Langmuir* **1995**, *11*, 1215.
[34] J. D. Legrange, J. L. Markham, C. R. Kurkjian, *Langmuir* **1993**, *9*, 1749.
[35] R. W. P. Fairbank, M. J. Wirth, *J. Chromatogr. A* **1999**, *830*, 285.
[36] R. W. Wang, S. L. Wunder, *Langmuir* **2000**, *16*, 5008.
[37] M. L. Hair, C. P. Tripp, *Colloids Surf. A* **1995**, *105*, 95.
[38] R. R. Rye, G. C. Nelson, M. T. Dugger, *Langmuir* **1997**, *13*, 2965.
[39] R. R. Rye, *Langmuir* **1997**, *13*, 2588.
[40] M. J. Stevens, *Langmuir* **1999**, *15*, 2773.
[41] R. Banga, J. Yarwood, A. M. Morgan, B. Evans, J. Kells, *Thin Solid Films* **1996**, *285*, 261.
[42] I. M. Tidswell, B. M. Ocko, P. S. Pershan, S. R. Wasserman, G. M. Whitesides, J. D. Axe, *Phys. Rev. B* **1990**, *41*, 1111.
[43] I. M. Tidswell, T. A. Rabedeau, P. S. Pershan, S. D. Kosowsky, J. P. Folkers, G. M. Whitesides, *J. Chem. Phys.* **1991**, *95*, 2854.
[44] M. Fujii, S. Sugisawa, K. Fukada, T. Kato, T. Seimiya, *Langmuir* **1995**, *11*, 405.
[45] Fujii et al. reported an occupied area of 0.43 nm^2 per OTS chain, but extensively dried the substrate prior to self-assembly. This could explain the high surface area per OTS chain and the observed low ellipsometric thickness.
[46] S. W. Barton, A. Goudot, F. Rondelez, *Langmuir* **1991**, *7*, 1029.
[47] K. Kojio, S. R. Ge, A. Takahara, T. Kajiyama, *Langmuir* **1998**, *14*, 971.
[48] K. Kojio, A. Takahara, K. Omote, T. Kajiyama, *Langmuir* **2000**, *16*, 3932.
[49] R. Maoz, J. Sagiv, D. Degenhardt, H. Mohwald, P. Quint, *Supramol. Sci.* **1995**, *2*, 9.
[50] A. Baptiste, A. Gibaud, J. F. Bardeau, K. Wen, R. Maoz, J. Sagiv, B. M. Ocko, *Langmuir* **2002**, *18*, 3916.

[51] Y. L. Wang, M. Lieberman, *Langmuir* **2003**, *19*, 1159.
[52] M. E. McGovern, K. M. R. Kallury, M. Thompson, *Langmuir* **1994**, *10*, 3607.
[53] T. Ohtake, N. Mino, K. Ogawa, *Langmuir* **1992**, *8*, 2081.
[54] K. Mathauer, C. W. Frank, *Langmuir* **1993**, *9*, 3002.
[55] K. Mathauer, C. W. Frank, *Langmuir* **1993**, *9*, 3446.
[56] K. Bierbaum, M. Grunze, A. A. Baski, L. F. Chi, W. Schrepp, H. Fuchs, *Langmuir* **1995**, *11*, 2143.
[57] R. Banga, J. Yarwood, A. M. Morgan, B. Evans, J. Kells, *Langmuir* **1995**, *11*, 4393.
[58] B. C. Bunker, R. W. Carpick, R. A. Assink, M. L. Thomas, M. G. Hankins, J. A. Voigt, D. Sipola, M. P. de Boer, G. L. Gulley, *Langmuir* **2000**, *16*, 7742.
[59] N. Rozlosnik, M. C. Gerstenberg, N. B. Larsen, *Langmuir* **2003**, *19*, 1182.
[60] T. Vallant, H. Brunner, U. Mayer, H. Hoffmann, T. Leitner, R. Resch, G. Friedbacher, *J. Phys. Chem. B* **1998**, *102*, 7190.
[61] T. Leitner, G. Friedbacher, T. Vallant, H. Brunner, U. Mayer, H. Hoffmann, *Mikrochim. Acta* **2000**, *133*, 331.
[62] M. Reiniger, B. Basnar, G. Friedbacher, M. Schleberger, *Surf. Interface Anal.* **2002**, *25*, 85.
[63] Y. Liu, L. K. Wolf, M. C. Messmer, *Langmuir* **2001**, *17*, 4329.
[64] T. Balgar, R. Bautista, N. Hartmann, E. Hasselbrink, *Surf. Sci.* **2003**, *532*, 963.
[65] J. V. Davidovits, V. Pho, P. Silberzan, M. Goldmann, *Surf. Sci.* **1996**, *352*, 369.
[66] C. Carraro, O. W. Yauw, M. M. Sung, R. Maboudian, *J. Phys. Chem. B* **1998**, *102*, 4441.
[67] M. M. Sung, C. Carraro, O. W. Yauw, Y. Kim, R. Maboudian, *J. Phys. Chem. B* **2000**, *104*, 1556.
[68] A. Glaser, J. Foisner, G. Friedbacher, H. Hoffmann, *Anal. Bioanal. Chem.* **2004**, *379*, 653.
[69] T. Vallant, J. Kattner, H. Brunner, U. Mayer, H. Hoffmann, *Langmuir* **1999**, *15*, 5339.
[70] A. G. Richter, C. J. Yu, A. Datta, J. Kmetko, P. Dutta, *Colloids Surf. A* **2002**, *198*, 3.
[71] R. Bautista, N. Hartmann, E. Hasselbrink, *Langmuir* **2003**, *19*, 6590.
[72] M. Goldmann, J. V. Davidovits, P. Silberzan, *Thin Solid Films* **1998**, *329*, 166.
[73] J. B. Brzoska, N. Shahidzadeh, F. Rondelez, *Nature* **1992**, *360*, 719.
[74] J. B. Brzoska, I. Benazouz, F. Rondelez, *Langmuir* **1994**, *10*, 4367.
[75] A. N. Parikh, D. L. Allara, I. B. Azouz, F. Rondelez, *J. Phys. Chem.* **1994**, *98*, 7577.
[76] A. Glaser, J. Foisner, H. Hoffmann, G. Friedbacher, *Langmuir* **2004**, *20*, 5599.
[77] M. CalistriYeh, E. J. Kramer, R. Sharma, W. Zhao, M. H. Rafailovich, J. Sokolov, J. D. Brock, *Langmuir* **1996**, *12*, 2747.
[78] U. Srinivasan, M. R. Houston, R. T. Howe, R. Maboudian, *J. Microelectromech. Syst.* **1998**, *7*, 252.
[79] R. W. Wang, G. Baran, S. L. Wunder, *Langmuir* **2000**, *16*, 6298.
[80] R. W. Wang, S. L. Wunder, *J. Phys. Chem. B* **2001**, *105*, 173.
[81] D. Devaprakasam, S. Sampath, S. K. Biswas, *Langmuir* **2004**, *20*, 1329.
[82] N. Tillman, A. Ulman, J. S. Schildkraut, T. L. Penner, *J. Am. Chem. Soc.* **1988**, *110*, 6136.
[83] N. Tillman, A. Ulman, T. L. Penner, *Langmuir* **1989**, *5*, 101.
[84] M. R. Linford, C. E. D. Chidsey, *J. Am. Chem. Soc.* **1993**, *115*, 12631.
[85] M. R. Linford, P. Fenter, P. M. Eisenberger, C. E. D. Chidsey, *J. Am. Chem. Soc.* **1995**, *117*, 3145.
[86] S. R. Wasserman, Y. T. Tao, G. M. Whitesides, *Langmuir* **1989**, *5*, 1074.
[87] J. Rühe, V. J. Novotny, K. K. Kanazawa, T. Clarke, G. B. Street, *Langmuir* **1993**, *9*, 2383.
[88] X. D. Xiao, J. Hu, D. H. Charych, M. Salmeron, *Langmuir* **1996**, *12*, 235.
[89] X. D. Xiao, G. Y. Liu, D. H. Charych, M. Salmeron, *Langmuir* **1995**, *11*, 1600.
[90] S. Ren, S. R. Yang, Y. P. Zhao, J. F. Zhou, T. Xu, W. M. Liu, *Tribol. Lett.* **2002**, *13*, 233.
[91] D. G. Kurth, T. Bein, *Langmuir* **1993**, *9*, 2965.
[92] T. T.-T. Li, M. J. Weaver, *J. Am. Chem. Soc.* **1984**, *106*, 6107.
[93] B. Zhao, D. Mulkey, W. J. Brittain, Z. H. Chen, M. D. Foster, *Langmuir* **1999**, *15*, 6856.
[94] O. Gershevitz, C. N. Sukenik, *J. Am. Chem. Soc.* **2004**, *126*, 482.
[95] C. T. Konek, M. J. Musorrafiti, H. A. Al-Abadleh, P. A. Bertin, S. T. Nguyen, F. M. Geiger, *J. Am. Chem. Soc.* **2004**, *126*, 11754.
[96] Y. Barness, O. Gershevitz, M. Sekar, C. N. Sukenik, *Langmuir* **2000**, *16*, 247.
[97] R. Maoz, H. Cohen, J. Sagiv, *Langmuir* **1998**, *14*, 5988.
[98] Y. L. Wang, T. J. Su, R. Green, Y. Q. Tang, D. Styrkas, T. N. Danks, R. Bolton, J. R. Liu, *Chem. Commun.* **2000**, 587.
[99] J. S. Park, G. S. Lee, Y. J. Lee, Y. S. Park, K. B. Yoon, *J. Am. Chem. Soc.* **2002**, *124*, 13366.
[100] N. Tillman, A. Ulman, J. F. Elman, *Langmuir* **1989**, *5*, 1020.
[101] M. K. Chaudhury, G. M. Whitesides, *Science* **1992**, *255*, 1230.
[102] N. Balachander, C. N. Sukenik, *Langmuir* **1990**, *6*, 1621.
[103] Y. W. Lee, J. Reedmundell, C. N. Sukenik, J. E. Zull, *Langmuir* **1993**, *9*, 3009.
[104] K. Ogawa, N. Mino, H. Tamura, M. Hatada, *Langmuir* **1990**, *6*, 1807.
[105] L. A. Wenzler, G. L. Moyes, G. N. Raikar, R. L. Hansen, J. M. Harris, T. P. Beebe, L. L. Wood, S. S. Saavedra, *Langmuir* **1997**, *13*, 3761.
[106] J. A. Chupa, S. T. Xu, R. F. Fischetti, R. M. Strongin, J. P. McCauley, A. B. Smith, J. K. Blasie, L. J. Peticolas, J. C. Bean, *J. Am. Chem. Soc.* **1993**, *115*, 4383.
[107] M. V. Baker, J. D. Watling, *Langmuir* **1997**, *13*, 2027.
[108] M. T. Lee, G. S. Ferguson, *Langmuir* **2001**, *17*, 762.
[109] V. V. Tsukruk, L. M. Lander, W. J. Brittain, *Langmuir* **1994**, *10*, 996.
[110] G. E. Fryxell, P. C. Rieke, L. L. Wood, M. H. Engelhard, R. E. Williford, G. L. Graff, A. A. Campbell, R. J. Wiacek, L. Lee, A. Halverson, *Langmuir* **1996**, *12*, 5064.
[111] S. Onclin, A. Mulder, J. Huskens, B. J. Ravoo, D. N. Reinhoudt, *Langmuir* **2004**, *20*, 5460.
[112] K. Bierbaum, M. Kinzler, C. Wöll, M. Grunze, G. Hähner, S. Heid, F. Effenberger, *Langmuir* **1995**, *11*, 512.
[113] S. P. Zhdanov, L. S. Kosheleva, T. I. Titova, *Langmuir* **1987**, *3*, 960.
[114] K. M. Chen, W. B. Caldwell, C. A. Mirkin, *J. Am. Chem. Soc.* **1993**, *115*, 1193.
[115] D. Q. Li, B. I. Swanson, *Langmuir* **1993**, *9*, 3341.
[116] P. A. Heiney, K. Gruneberg, J. Y. Fang, C. Dulcey, R. Shashidhar, *Langmuir* **2000**, *16*, 2651.
[117] J. Y. Fang, M. S. Chen, R. Shashidhar, *Langmuir* **2001**, *17*, 1549.
[118] S. Flink, F. C. J. M. van Veggel, D. N. Reinhoudt, *J. Phys. Org. Chem.* **2001**, *14*, 407.
[119] A. V. Krasnoslobodtsev, S. N. Smirnov, *Langmuir* **2002**, *18*, 3181.
[120] Z. Zhang, R. Hu, Z. Liu, *Langmuir* **2000**, *16*, 1158.
[121] R. Rosario, D. Gust, M. Hayes, F. Jahnke, J. Springer, A. A. Garcia, *Langmuir* **2002**, *18*, 8062.
[122] B. C. Bunker, B. I. Kim, J. E. Houston, R. Rosario, A. A. Garcia, M. Hayes, D. Gust, S. T. Picraux, *Nano Lett.* **2003**, *3*, 1723.
[123] M. H. Hu, S. Noda, T. Okubo, Y. Yamaguchi, H. Komiyama, *Appl. Surf. Sci.* **2001**, *181*, 307.
[124] J. Y. Tseng, M. H. Lin, L. K. Chau, *Colloids Surf. A* **2001**, *182*, 239.

[125] E. Cano-Serrano, J. M. Campos-Martin, J. L. G. Fierro, *Chem. Commun.* **2003**, 246.

[126] Z. C. Liu, Q. G. He, P. F. Xiao, B. Liang, J. X. Tan, N. Y. He, Z. H. Lu, *Mater. Chem. Phys.* **2003**, *82*, 301.

[127] I. Luzinov, D. Julthongpiput, A. Liebmann-Vinson, T. Cregger, M. D. Foster, V. V. Tsukruk, *Langmuir* **2000**, *16*, 504.

[128] A. Kulak, Y. J. Lee, Y. S. Park, K. B. Yoon, *Angew. Chem.* **2000**, *112*, 980; *Angew. Chem. Int. Ed.* **2000**, *39*, 950.

[129] S. Busse, M. DePaoli, G. Wenz, S. Mittler, *Sens. Actuators B* **2001**, *80*, 116.

[130] O. Prucker, J. Rühe, *Macromolecules* **1998**, *31*, 592.

[131] D. H. Jung, I. J. Park, Y. K. Choi, S. B. Lee, H. S. Park, J. Rühe, *Langmuir* **2002**, *18*, 6133.

[132] B. Zhao, W. J. Brittain, *J. Am. Chem. Soc.* **1999**, *121*, 3557.

[133] M. Husseman, E. E. Malmstrom, M. McNamara, M. Mate, D. Mecerreyes, D. G. Benoit, J. L. Hedrick, P. Mansky, E. Huang, T. P. Russel, C. J. Hawker, *Macromolecules* **1999**, *32*, 1424.

[134] X. Huang, M. J. Wirth, *Macromolecules* **1999**, *32*, 1694.

[135] K. Matyjaszewski, P. J. Miller, N. Shukla, B. Immaraporn, A. Gelman, B. B. Luokala, T. M. Siclovan, G. Kickelbick, T. Vallant, H. Hoffmann, T. Pakula, *Macromolecules* **1999**, *32*, 8716.

[136] E. Lindner, E. Arias, *Langmuir* **1992**, *8*, 1195.

[137] C. P. Tripp, R. P. N. Veregin, M. L. Hair, *Langmuir* **1993**, *9*, 3518.

[138] A. Papra, N. Gadegaard, N. B. Larsen, *Langmuir* **2001**, *17*, 1457.

[139] Z. Yang, J. A. Galloway, H. Yu, *Langmuir* **1999**, *15*, 8405.

[140] Y.-H. M. Chan, R. Schweiss, C. Werner, M. Grunze, *Langmuir* **2003**, *19*, 7380.

[141] R. J. Collins, I. T. Bae, D. A. Scherson, C. N. Sukenik, *Langmuir* **1996**, *12*, 5509.

[142] S. Kato, C. Pac, *Langmuir* **1998**, *14*, 2372.

[143] C. M. Yam, A. K. Kakkar, *Langmuir* **1999**, *15*, 3807.

[144] R. Maoz, S. Matlis, E. DiMasi, B. M. Ocko, J. Sagiv, *Nature* **1996**, *384*, 150.

[145] R. Maoz, J. Sagiv, *Adv. Mater.* **1998**, *10*, 580.

[146] H. Lee, L. J. Kepley, H. G. Hong, T. E. Mallouk, *J. Am. Chem. Soc.* **1988**, *110*, 618.

[147] H. Lee, L. J. Kepley, H. G. Hong, S. Akhter, T. E. Mallouk, *J. Phys. Chem.* **1988**, *92*, 2597.

[148] D. Q. Li, M. A. Ratner, T. J. Marks, C. H. Zhang, J. Yang, G. K. Wong, *J. Am. Chem. Soc.* **1990**, *112*, 7389.

[149] A. K. Kakkar, S. Yitzchaik, S. B. Roscoe, F. Kubota, D. S. Allan, T. J. Marks, W. P. Lin, G. K. Wong, *Langmuir* **1993**, *9*, 388.

[150] S. Yitzchaik, S. B. Roscoe, A. K. Kakkar, D. S. Allan, T. J. Marks, Z. Y. Xu, T. G. Zhang, W. P. Lin, G. K. Wong, *J. Phys. Chem.* **1993**, *97*, 6958.

[151] S. B. Roscoe, S. Yitzchaik, A. K. Kakkar, T. J. Marks, *Langmuir* **1994**, *10*, 1337.

[152] S. Yitzchaik, T. J. Marks, *Acc. Chem. Res.* **1996**, *29*, 197.

[153] S. B. Roscoe, A. K. Kakkar, T. J. Marks, A. Malik, M. K. Durbin, W. P. Lin, G. K. Wong, P. Dutta, *Langmuir* **1996**, *12*, 4218.

[154] M. E. van der Boom, G. Evmenenko, C. J. Yu, P. Dutta, T. J. Marks, *Langmuir* **2003**, *19*, 10531.

[155] N. J. van der Veen, S. Flink, M. A. Deij, R. J. M. Egberink, F. C. J. M. van Veggel, D. N. Reinhoudt, *J. Am. Chem. Soc.* **2000**, *122*, 6112.

[156] W. Dulkeith, A. C. Morteani, T. Niedereichholtz, T. A. Klar, J. Feldmann, S. A. Levi, F. C. J. M. van Veggel, D. N. Reinhoudt, M. Möller, D. Gittins, *Phys. Rev. Lett.* **2002**, *89*, 203002.

[157] R. Chance, A. Prock, R. Silbey, *Adv. Chem. Phys.* **1978**, *37*, 1.

[158] J. Kummerlen, A. Leitner, H. Brunner, F. R. Aussenegg, A. Wokaun, *Mol. Phys.* **1993**, *80*, 1031.

[159] J. Enderlein, *Chem. Phys.* **1999**, *247*, 1.

[160] S. Reese, M. A. Fox, *J. Phys. Chem. B* **1998**, *102*, 9820.

[161] L. N. Gao, Y. Fang, X. P. Wen, Y. G. Li, D. D. Hu, *J. Phys. Chem. B* **2004**, *108*, 1207.

[162] M. Ayadim, J. L. H. Jiwan, A. P. de Silva, J. P. Soumillion, *Tetrahedron Lett.* **1996**, *37*, 7039.

[163] D. W. J. McCallien, P. L. Burn, H. L. Anderson, *J. Chem. Soc. Perkin Trans. 1* **1997**, 2581.

[164] D. L. Pilloud, C. C. Moser, K. S. Reddy, P. L. Dutton, *Langmuir* **1998**, *14*, 4809.

[165] A. Bianco, F. Gasparrini, M. Maggini, D. Misiti, A. Polese, M. Prato, G. Scorrano, C. Toniolo, C. Villani, *J. Am. Chem. Soc.* **1997**, *119*, 7550.

[166] D. Q. Li, M. Ma, *Sens. Actuators B* **2000**, *69*, 75.

[167] C. M. Rudzinski, A. M. Young, D. G. Nocera, *J. Am. Chem. Soc.* **2002**, *124*, 1723.

[168] S. Flink, F. C. J. M. van Veggel, D. N. Reinhoudt, *Chem. Commun.* **1999**, 2229.

[169] M. Crego-Calama, D. N. Reinhoudt, *Adv. Mater.* **2001**, *13*, 1171.

[170] L. Basabe-Desmonts, J. Beld, R. S. Zimmerman, J. Hernando, P. Mela, M. F. García Parajó, N. F. Van Hulst, A. Van den Berg, D. N. Reinhoudt, M. Crego-Calama, *J. Am. Chem. Soc.* **2004**, *126*, 7293.

[171] E. Brasola, F. Mancin, E. Rampazzo, P. Tecilla, U. Tonellato, *Chem. Commun.* **2003**, 3026.

[172] M. C. Pirrung, *Angew. Chem.* **2002**, *114*, 1326; *Angew. Chem. Int. Ed.* **2002**, *41*, 1276.

[173] D. S. Wilson, S. Nock, *Angew. Chem.* **2003**, *115*, 510; *Angew. Chem. Int. Ed.* **2003**, *42*, 494.

[174] T. P. Sullivan, W. T. S. Huck, *Eur. J. Org. Chem.* **2003**, 17.

[175] S. Margel, O. Sivan, Y. Dolitzky, *Langmuir* **1991**, *7*, 2317.

[176] Y. Belosludtsev, B. Iverson, S. Lemeshko, R. Eggers, R. Wiese, S. Lee, T. Powdrill, M. Hogan, *Anal. Biochem.* **2001**, *292*, 250.

[177] N. Zammatteo, L. Jeanmart, S. Hamels, S. Courtois, P. Louette, L. Hevesi, J. Remacle, *Anal. Biochem.* **2000**, *280*, 143.

[178] S. Tasker, G. Matthijs, M. C. Davies, C. J. Roberts, E. H. Schacht, S. J. B. Tendler, *Langmuir* **1996**, *12*, 6436.

[179] D. Barnes-Seeman, S. B. Park, A. N. Koehler, S. L. Schreiber, *Angew. Chem.* **2003**, *115*, 2478; *Angew. Chem. Int. Ed.* **2003**, *42*, 2376.

[180] N. Kanoh, S. Kumashiro, S. Simizu, Y. Kondoh, S. Hatakeyama, H. Tashiro, H. Osada, *Angew. Chem.* **2003**, *115*, 5742; *Angew. Chem. Int. Ed.* **2003**, *42*, 5584.

[181] H. G. Hong, P. W. Bohn, S. G. Sligar, *Anal. Chem.* **1993**, *65*, 1635.

[182] H. G. Hong, M. Jiang, S. G. Sligar, P. W. Bohn, *Langmuir* **1994**, *10*, 153.

[183] G. MacBeath, A. N. Koehler, S. L. Schreiber, *J. Am. Chem. Soc.* **1999**, *121*, 7967.

[184] V. Benoit, A. Steel, M. Torres, Y. Y. Lu, H. J. Yang, J. Cooper, *Anal. Chem.* **2001**, *73*, 2412.

[185] M. J. O'Donnell, K. Tang, H. Koster, C. L. Smith, C. R. Cantor, *Anal. Chem.* **1997**, *69*, 2438.

[186] M. M. A. Sekar, P. D. Hampton, T. Buranda, G. P. Lopez, *J. Am. Chem. Soc.* **1999**, *121*, 5135.

[187] R. Benters, C. M. Niemeyer, D. Wöhrle, *ChemBioChem* **2001**, *2*, 686.

[188] M. Köhn, R. Wacker, C. Peters, H. Schröder, L. Soulère, R. Breinbauer, C. M. Niemeyer, H. Waldmann, *Angew. Chem.* **2003**, *115*, 6010; *Angew. Chem. Int. Ed.* **2003**, *42*, 5830.

[189] M. B. Soellner, K. A. Dickson, B. L. Nilsson, R. T. Raines, *J. Am. Chem. Soc.* **2003**, *125*, 11790.

[190] D. Leipert, D. Nopper, M. Bauser, G. Gauglitz, G. Jung, *Angew. Chem.* **1998**, *110*, 3503; *Angew. Chem. Int. Ed.* **1998**, *37*, 3308.

[191] M. Elbs, R. Brock, *Anal. Chem.* **2003**, *75*, 4793.

[192] R. A. Potyrailo, R. C. Conrad, A. D. Ellington, G. M. Hieftje, *Anal. Chem.* **1998**, *70*, 3419.

[193] G. MacBeath, S. L. Schreiber, *Science* **2000**, *289*, 1760.

[194] C. M. Salisbury, D. J. Maly, J. A. Ellman, *J. Am. Chem. Soc.* **2002**, *124*, 14868.

[195] D. L. Pilloud, F. Rabanal, B. R. Gibney, R. S. Farid, P. L. Dutton, C. C. Moser, *J. Phys. Chem. B* **1998**, *102*, 1926.

[196] Y. H. Rogers, P. Jiang-Baucom, Z. J. Huang, V. Bogdanov, S. Anderson, M. T. Boyce-Jacino, *Anal. Biochem.* **1999**, *266*, 23.

[197] P. S. Stayton, J. M. Olinger, M. Jiang, P. W. Bohn, S. G. Sligar, *J. Am. Chem. Soc.* **1992**, *114*, 9298.

[198] P. J. Hergenrother, K. M. Depew, S. L. Schreiber, *J. Am. Chem. Soc.* **2000**, *122*, 7849.

[199] M. C. Pirrung, J. D. Davis, A. L. Odenbaugh, *Langmuir* **2000**, *16*, 2185.

[200] D. S. Ginger, H. Zhang, C. A. Mirkin, *Angew. Chem.* **2004**, *116*, 30; *Angew. Chem. Int. Ed.* **2004**, *43*, 30.

[201] A. Y. Fadeev, T. J. McCarthy, *Langmuir* **1999**, *15*, 7238.

[202] F. Q. Fan, C. Maldarelli, A. Couzis, *Langmuir* **2003**, *19*, 3254.

[203] K. R. Finnie, R. G. Nuzzo, *Langmuir* **2001**, *17*, 1250.

[204] J. P. Lee, Y. J. Jang, M. M. Sung, *Adv. Funct. Mater.* **2003**, *13*, 873.

[205] N. Kumar, C. Maldarelli, C. Steiner, A. Couzis, *Langmuir* **2001**, *17*, 7789.

[206] J. Buseman-Williams, J. C. Berg, *Langmuir* **2004**, *20*, 2026.

[207] Z. D. Xiao, C. Z. Cai, A. Mayeux, A. Milenkovic, *Langmuir* **2002**, *18*, 7728.

[208] C. M. Yam, A. Mayeux, A. Milenkovic, C. Z. Cai, *Langmuir* **2002**, *18*, 10274.

[209] B. J. Hong, J. Y. Shim, S. J. Oh, J. W. Park, *Langmuir* **2003**, *19*, 2357.

[210] C. S. Dulcey, J. H. Georger, V. Krauthamer, D. A. Stenger, T. L. Fare, J. M. Calvert, *Science* **1991**, *252*, 551.

[211] D. A. Stenger, J. H. Georger, C. S. Dulcey, J. J. Hickman, A. S. Rudolph, T. B. Nielsen, S. M. McCort, J. M. Calvert, *J. Am. Chem. Soc.* **1992**, *114*, 8435.

[212] N. Saito, K. Hayashi, H. Sugimura, O. Takai, N. Nakagiri, *Chem. Phys. Lett.* **2001**, *349*, 172.

[213] K. Hayashi, N. Saito, H. Sugimura, O. Takai, N. Nakagiri, *Langmuir* **2002**, *18*, 7469.

[214] H. Sugimura, K. Ushiyama, A. Hozumi, O. Takai, *Langmuir* **2000**, *16*, 885.

[215] H. Sugimura, T. Hanji, O. Takai, T. Masuda, H. Misawa, *Electrochim. Acta* **2001**, *47*, 103.

[216] N. Saito, H. Haneda, T. Sekiguchi, N. Ohashi, I. Sakaguchi, K. Koumoto, *Adv. Mater.* **2002**, *14*, 418.

[217] Y. Masuda, W. S. Seo, K. Koumoto, *Langmuir* **2001**, *17*, 4876.

[218] J. P. Lee, M. M. Sung, *J. Am. Chem. Soc.* **2004**, *126*, 28.

[219] U. Jonas, A. del Campo, C. Krüger, G. Glasser, D. Boos, *Proc. Natl. Acad. Sci. USA* **2002**, *99*, 5034.

[220] M. Nakagawa, K. Ichimura, *Colloids Surf. A* **2002**, *204*, 1.

[221] M. C. Pirrung, *Chem. Rev.* **1997**, *97*, 473.

[222] S. P. A. Fodor, J. L. Read, M. C. Pirrung, L. Stryer, A. T. Lu, D. Solas, *Science* **1991**, *251*, 767.

[223] A. Pease, D. Solas, E. Sullivan, M. Cronin, C. Holmes, S. Fodor, *Proc. Natl. Acad. Sci. USA* **1994**, *91*, 5022.

[224] G. McGall, J. Labadie, P. Brock, G. Wallraff, T. Nguyen, W. Hinsberg, *Proc. Natl. Acad. Sci. USA* **1996**, *93*, 13555.

[225] G. H. McGall, A. D. Barone, M. Diggelmann, S. P. A. Fodor, E. Gentalen, N. Ngo, *J. Am. Chem. Soc.* **1997**, *119*, 5081.

[226] S. L. Brandow, M. S. Chen, R. Aggarwal, C. S. Dulcey, J. M. Calvert, W. J. Dressick, *Langmuir* **1999**, *15*, 5429.

[227] B. Zhao, J. S. Moore, D. J. Beebe, *Science* **2001**, *291*, 1023.

[228] B. Zhao, J. S. Moore, D. J. Beebe, *Anal. Chem.* **2002**, *74*, 4259.

[229] B. Zhao, N. O. L. Viernes, J. S. Moore, D. J. Beebe, *J. Am. Chem. Soc.* **2002**, *124*, 5284.

[230] T. Balgar, S. Franzka, N. Hartmann, E. Hasselbrink, *Langmuir* **2004**, *20*, 3525.

[231] M. J. Lercel, R. C. Tiberio, P. F. Chapman, H. G. Craighead, C. W. Sheen, A. N. Parikh, D. L. Allara in *Proceedings of the 16th international symposium on electron, ion, and photon beams*, *Vol. 11*, AVS, San Diego, California (USA), **1993**, 2823.

[232] M. J. Lercel, G. F. Redinbo, F. D. Pardo, M. Rooks, R. C. Tiberio, P. Simpson, H. G. Craighead, C. W. Sheen, A. N. Parikh, D. L. Allara, *J. Vac. Sci. Technol. B* **1994**, *12*, 3663.

[233] P. M. StJohn, H. G. Craighead, *J. Vac. Sci. Technol. B* **1996**, *14*, 69.

[234] M. J. Lercel, H. G. Craighead, A. N. Parikh, K. Seshadri, D. L. Allara, *Appl. Phys. Lett.* **1996**, *68*, 1504.

[235] C. R. K. Marrian, F. K. Perkins, S. L. Brandow, T. S. Koloski, E. A. Dobisz, J. M. Calvert, *Appl. Phys. Lett.* **1994**, *64*, 390.

[236] C. K. Harnett, K. M. Satyalakshmi, H. G. Craighead, *Appl. Phys. Lett.* **2000**, *76*, 2466.

[237] T. Sato, D. G. Hasko, H. Ahmed, *J. Vac. Sci. Technol. B* **1997**, *15*, 45.

[238] K. H. Choi, J. P. Bourgoin, S. Auvray, D. Esteve, G. S. Duesberg, S. Roth, M. Burghard, *Surf. Sci.* **2000**, *462*, 195.

[239] R. Krupke, S. Malik, H. B. Weber, O. Hampe, M. M. Kappes, H. von Löhneysen, *Nano Lett.* **2002**, *2*, 1161.

[240] Y. J. Jung, Y. H. La, H. J. Kim, T. H. Kang, K. Ihm, K. J. Kim, B. Kim, J. W. Park, *Langmuir* **2003**, *19*, 4512.

[241] I. S. Maeng, J. W. Park, *Langmuir* **2003**, *19*, 4519.

[242] P. M. Mendes, S. Jacke, K. Critchley, J. Plaza, Y. Chen, K. Nikitin, R. E. Palmer, J. A. Preece, S. D. Evans, D. Fitzmaurice, *Langmuir* **2004**, *20*, 3766.

[243] X. J. Wang, W. C. Hu, R. Ramasubramaniam, G. H. Bernstein, G. Snider, M. Lieberman, *Langmuir* **2003**, *19*, 9748.

[244] A. Pallandre, K. Glinel, A. M. Jonas, B. Nysten, *Nano Lett.* **2004**, *4*, 365.

[245] R. L. Kubena, J. W. Ward, F. P. Stratton, R. J. Joyce, G. M. Atkinson, *J. Vac. Sci. Technol. B* **1991**, *9*, 3079.

[246] R. L. Kubena, R. J. Joyce, J. W. Ward, H. L. Garvin, F. P. Stratton, R. G. Brault, *J. Vac. Sci. Technol. B* **1988**, *6*, 353.

[247] P. C. Rieke, B. J. Tarasevich, L. L. Wood, M. H. Engelhard, D. R. Baer, G. E. Fryxell, C. M. John, D. A. Laken, M. C. Jaehnig, *Langmuir* **1994**, *10*, 619.

[248] E. T. Ada, L. Hanley, S. Etchin, J. Melngailis, W. J. Dressick, M.-S. Chen, J. M. Calvert, *J. Vac. Sci. Technol. B* **1995**, *13*, 2189.

[249] T. Schenkel, M. Schneider, M. Hattass, M. W. Newman, A. V. Barnes, A. V. Hamza, D. H. Schneider, R. L. Cicero, C. E. D. Chidsey, *J. Vac. Sci. Technol. B* **1998**, *16*, 3298.

[250] R. Younkin, K. K. Berggren, K. S. Johnson, M. Prentiss, D. C. Ralph, G. M. Whitesides, *Appl. Phys. Lett.* **1997**, *71*, 1261.

[251] D. Suh, J. K. Simons, J. W. Taylor, T. S. Koloski, J. M. Calvert in *Proceedings of the 16th international symposium on electron, ion, and photon beams*, *Vol. 11*, AVS, San Diego, California (USA), **1993**, 2850.

[252] W. J. Dressick, C. S. Dulcey, S. L. Brandow, H. Witschi, P. F. Neeley, *J. Vac. Sci. Technol. A* **1999**, *17*, 1432.

[253] Y. H. La, H. J. Kim, I. S. Maeng, Y. J. Jung, J. W. Park, K. J. Kim, T. H. Kang, B. Kim, *Langmuir* **2002**, *18*, 2430.

[254] Y. H. La, Y. J. Jung, H. J. Kim, T. H. Kang, K. Ihm, K. J. Kim, B. Kim, J. W. Park, *Langmuir* **2003**, *19*, 4390.

[255] X. M. Yang, R. D. Peters, T. K. Kim, P. F. Nealey, S. L. Brandow, M. S. Chen, L. M. Shirey, W. J. Dressick, *Langmuir* **2001**, *17*, 228.

[256] S. O. Kim, H. H. Solak, M. P. Stoykovich, N. J. Ferrier, J. J. de Pablo, P. F. Nealey, *Nature* **2003**, *424*, 411.

[257] Y. N. Xia, G. M. Whitesides, *Angew. Chem.* **1998**, *110*, 568; *Angew. Chem. Int. Ed.* **1998**, *37*, 551.

[258] Y. N. Xia, J. A. Rogers, K. E. Paul, G. M. Whitesides, *Chem. Rev.* **1999**, *99*, 1823.

[259] Y. N. Xia, M. Mrksich, E. Kim, G. M. Whitesides, *J. Am. Chem. Soc.* **1995**, *117*, 9576.

[260] P. M. S. John, H. G. Craighead, *Appl. Phys. Lett.* **1996**, *68*, 1022.

[261] D. Wang, S. G. Thomas, K. L. Wang, Y. Xia, G. M. Whitesides, *Appl. Phys. Lett.* **1997**, *70*, 1593.

[262] N. L. Jeon, K. Finnie, K. Branshaw, R. G. Nuzzo, *Langmuir* **1997**, *13*, 3382.
[263] K. R. Finnie, R. Haasch, R. G. Nuzzo, *Langmuir* **2000**, *16*, 6968.
[264] Y. Harada, G. S. Girolami, R. G. Nuzzo, *Langmuir* **2003**, *19*, 5104.
[265] T. Pfohl, J. H. Kim, M. Yasa, H. P. Miller, G. C. L. Wong, F. Bringezu, Z. Wen, L. Wilson, M. W. Kim, Y. Li, C. R. Safinya, *Langmuir* **2001**, *17*, 5343.
[266] N. L. Jeon, P. G. Clem, D. A. Payne, R. G. Nuzzo, *Langmuir* **1996**, *12*, 5350.
[267] C. E. Moran, C. Radloff, N. J. Halas, *Adv. Mater.* **2003**, *15*, 804.
[268] P. C. Hidber, W. Helbig, E. Kim, G. M. Whitesides, *Langmuir* **1996**, *12*, 1375.
[269] T. Auletta, B. Dordi, A. Mulder, A. Sartori, S. Onclin, C. M. Bruinink, M. Péter, C. A. Nijhuis, H. Beijleveld, H. Schönherr, G. J. Vancso, A. Casnati, R. Ungaro, B. J. Ravoo, J. Huskens, N. F. Van Hulst, D. N. Reinhoudt, *Angew. Chem.* **2004**, *116*, 373; *Angew. Chem. Int. Ed.* **2004**, *43*, 369.
[270] A. Mulder, S. Onclin, M. Péter, J. P. Hoogenboom, H. Beijleveld, J. ter Maat, M. F. García Parajó, B. J. Ravoo, J. Huskens, N. F. van Hulst, D. N. Reinhoudt, *Small* **2005**, *1*, 242.
[271] V. Mahalingam, S. Onclin, M. Péter, B. J. Ravoo, J. Huskens, D. N. Reinhoudt, *Langmuir* **2004**, *20*, 11756.
[272] Y. L. Loo, R. L. Willett, K. W. Baldwin, J. A. Rogers, *J. Am. Chem. Soc.* **2002**, *124*, 7654.
[273] E. Delamarche, M. Geissler, R. H. Magnuson, H. Schmid, B. Michel, *Langmuir* **2003**, *19*, 5892.
[274] E. Delamarche, M. Geissler, J. Vichiconti, W. S. Graham, P. A. Andry, J. C. Flake, P. M. Fryer, R. W. Nunes, B. Michel, E. J. O'Sullivan, H. Schmid, H. Wolf, R. L. Wisnieff, *Langmuir* **2003**, *19*, 5923.
[275] M. Geissler, H. Kind, P. Schmidt-Winkel, B. Michel, E. Delamarche, *Langmuir* **2003**, *19*, 6283.
[276] M. Geissler, H. Wolf, R. Stutz, E. Delamarche, U. W. Grummt, B. Michel, A. Bietsch, *Langmuir* **2003**, *19*, 6301.
[277] E. Delamarche, J. Vichiconti, S. A. Hall, M. Geissler, W. Graham, B. Michel, R. Nunes, *Langmuir* **2003**, *19*, 6567.
[278] S. Y. Chou, P. R. Krauss, P. J. Renstrom, *Science* **1996**, *272*, 85.
[279] P. Maury, M. Péter, V. Mahalingam, D. N. Reinhoudt, J. Huskens, *Adv. Funct. Mater.* **2005**, *15*, 451.
[280] S. Kramer, R. R. Fuierer, C. B. Gorman, *Chem. Rev.* **2003**, *103*, 4367.
[281] H. Sugimura, N. Nakagiri, N. Ichinose, *Appl. Phys. Lett.* **1995**, *66*, 3686.
[282] H. Sugimura, N. Nakagiri, *J. Am. Chem. Soc.* **1997**, *119*, 9226.
[283] H. Sugimura, T. Hanji, K. Hayashi, O. Takai, *Adv. Mater.* **2002**, *14*, 524.
[284] A. Inoue, T. Ishida, N. Choi, W. Mizutani, H. Tokumoto, *Appl. Phys. Lett.* **1998**, *73*, 1976.
[285] R. Maoz, E. Frydman, S. R. Cohen, J. Sagiv, *Adv. Mater.* **2000**, *12*, 424.
[286] R. Maoz, S. R. Cohen, J. Sagiv, *Adv. Mater.* **1999**, *11*, 55.
[287] R. Maoz, E. Frydman, S. R. Cohen, J. Sagiv, *Adv. Mater.* **2000**, *12*, 725.
[288] S. T. Liu, R. Maoz, G. Schmid, J. Sagiv, *Nano Lett.* **2002**, *2*, 1055.
[289] S. Hoeppener, R. Maoz, S. R. Cohen, L. F. Chi, H. Fuchs, J. Sagiv, *Adv. Mater.* **2002**, *14*, 1036.
[290] C. S. Liu, R. Maoz, J. Sagiv, *Nano Lett.* **2004**, *4*, 845.
[291] S. Hoeppener, R. Maoz, J. Sagiv, *Nano Lett.* **2003**, *3*, 761.
[292] D. Wouters, U. S. Schubert, *Langmuir* **2003**, *19*, 9033.
[293] Z. M. Fresco, I. Suez, S. A. Backer, J. M. J. Frechet, *J. Am. Chem. Soc.* **2004**, *126*, 8374.
[294] W. T. Müller, D. L. Klein, T. Lee, J. Clarke, P. L. McEuen, P. G. Schultz, *Science* **1995**, *268*, 272.
[295] R. D. Piner, J. Zhu, F. Xu, S. H. Hong, C. A. Mirkin, *Science* **1999**, *283*, 661.
[296] A. Ivanisevic, C. A. Mirkin, *J. Am. Chem. Soc.* **2001**, *123*, 7887.
[297] D. J. Pena, M. P. Raphael, J. M. Byers, *Langmuir* **2003**, *19*, 9028.
[298] H. Jung, R. Kulkarni, C. P. Collier, *J. Am. Chem. Soc.* **2003**, *125*, 12096.
[299] L. M. Demers, D. S. Ginger, S.-J. Park, Z. Li, S.-W. Chung, C. A. Mirkin, *Science* **2002**, *296*, 1836.
[300] H. Jung, C. K. Dalal, S. Kuntz, R. Shah, C. P. Collier, *Nano Lett.* **2004**, *4*, 2171.
[301] J. H. Lim, D. S. Ginger, K. B. Lee, J. Heo, J. M. Nam, C. A. Mirkin, *Angew. Chem.* **2003**, *115*, 2411; *Angew. Chem. Int. Ed.* **2003**, *42*, 2309.