TOPICAL REVIEW

Self-assembled monolayers: from 'simple' model systems to biofunctionalized interfaces

Frank Schreiber

Physical and Theoretical Chemistry Laboratory, University of Oxford, South Parks Road, Oxford OX1 3QZ, UK

E-mail: frank.schreiber@chem.ox.ac.uk

Abstract
We review recent developments in the area of self-assembled monolayers (SAMs) and their applications. First, we discuss issues related to the structure, the phase transitions, the phase diagram, and the growth dynamics. We explain how the internal degrees of freedom and the multiple interactions involved can lead to a fairly rich phase behaviour even for systems which are commonly considered 'simple' model systems. Then we discuss selected problems for more complex SAM-based systems, including SAMs as substrates for growth, SAMs and molecular electronics, electrochemical applications, and 'switchable' SAMs, as well as the use of SAMs for biofunctionalized surfaces and lateral structuring.

(Some figures in this article are in colour only in the electronic version)

Contents

1. Introduction

The area of soft matter and molecular materials has developed into a strong branch of condensed matter research, and continues to attract growing attention. The variety of systems is immense, and due to the synthetic capabilities of organic chemistry there is hardly any limitation on the creation of new materials.

From a physical perspective, *inter alia*, the internal degrees of freedom and the competition of multiple interactions (including entropic contributions) are important characteristics. These typically result in a fairly rich and interesting phase behaviour and multiple length and timescales.

In thin films, additional issues related to the reduced dimensionality can come into play, and, again, there is a wide variety of systems, from Langmuir films (consisting of amphiphilic molecules spread on a liquid surface such as water [1, 2]) to Langmuir–Blodgett (LB) films (prepared by transferring Langmuir films onto a solid substrate [3]) and to films prepared by organic molecular beam deposition (OMBD) in vacuum [4], similar to evaporation techniques for inorganic materials. Organic thin films are, of course, not a discovery of the late 20th century, but were used in ancient times as soap films and other applications. For an account of the history as well as on the background of various forms of organic thin films, we refer to [1, 3, 6].

The term self-assembly is now widely used, which occasionally causes confusion. In a general sense, it may be defined as the spontaneous formation of complex hierarchical structures from pre-designed building blocks, typically involving multiple energy scales and multiple degrees of freedom. Specifically, self-assembled monolayers are ordered molecular assemblies that are formed spontaneously by the adsorption of a surfactant with a specific affinity of its headgroup to a substrate. They are usually prepared from solution, although some systems can be prepared from the vapour as well. We note that both preparation routes allow also for coating of arbitrarily shaped and not only planar geometries. Figure 1 shows a schematic diagram, including the constituents of a SAM molecule (headgroup, chain or backbone, endgroup). The headgroup–substrate 'pair' is typically used to define the individual SAM system. Popular examples are thiols (R–SH, where R denotes the rest of the molecule) on Au(111) [7] or silane-based systems on SiO_2 [8].

The discovery of SAMs and in particular the identification of the thiol/Au route has essentially transformed surface chemistry and also opened a new area for physically oriented groups. It has brought together the study of well defined inorganic surfaces and organic species, which from a physics perspective were previously often considered rather undefined. The great flexibility of the concept of SAMs brought about by the wide choice of endgroups which can be anchored to the substrate has led to a broad range of applications of SAMs including important developments in the area of biotechnology.

Twenty years after the pioneering work of Nuzzo and Allara on thiols on gold the area is still growing and getting more diverse. Thus, in a review with limited space such as the present one, it cannot be our goal to give a complete and exhaustive overview. We rather provide an update on recent developments in selected areas, based on our earlier, more complete review from 2000 [6]. Other reviews of earlier work can be found in [3, 5, 8–18], in some cases from a more chemical or technique-oriented perspective. We also try to indicate unresolved issues as well as some future directions. This selection is inevitably a personal and unbalanced one, and we apologize for omissions.
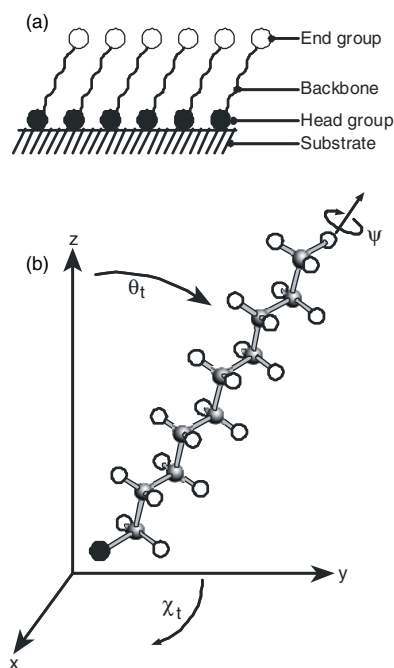
Figure 1. (a) Schematic diagram of a SAM ('standing-up' structure). The shaded circle indicates a chemisorbing headgroup and the open circle an endgroup, which can be chosen from a variety of chemical functionalities. (b) Typical SAM-forming molecule (decanethiol) with the angular degrees of freedom for an all-*trans* chain, tilt angle (θ_t), tilt direction (χ_t), and twist (ψ).

We will review a few general issues and recent progress from two angles. In section 2 we discuss fundamental issues related to 'simple' SAMs, their structure, phase diagram, phase transitions, and growth dynamics. Section 3 is devoted to a discussion of various ways to employ SAMs for functionalized surfaces, from SAMs as substrates for film growth to biorelated use of SAMs. For these applications, details of the monolayer structure itself are not in the focus (although, in fact, they frequently do matter), but the SAM is used as a 'vehicle' to produce a desired functionality. Some conclusions are given in section 4.

2. 'Simple' SAMs

In the context of the basic issues of structure, phase transitions, and growth of monolayers, typical fundamental questions are the following.

(1) Which types of structure and phase are formed and which parameters characterize the order (packing density; long-range versus local order; symmetry)? This refers to the headgroup–substrate binding structure as well as to the chain structure (tilt).
(2) In which way does the order appear and disappear (e.g., as a function of coverage or temperature) and what is the nature of the transitions?
(3) In which way do the various degrees of freedom and the different constituents of the molecule (headgroup, chain or backbone, endgroup) have an impact on the growth and the structure?
(4) What are the driving forces of self-assembly? What determines the growth kinetics and the growth regimes? What are the 'internal' (e.g., chain length or substrate orientation) and the 'external' (e.g., temperature) control parameters?

Various molecule–substrate systems have been used for SAMs. We will focus on the two most popular systems, which exhibit a different binding route and, consequently, different structural motifs, different mobility, and different growth behaviour.
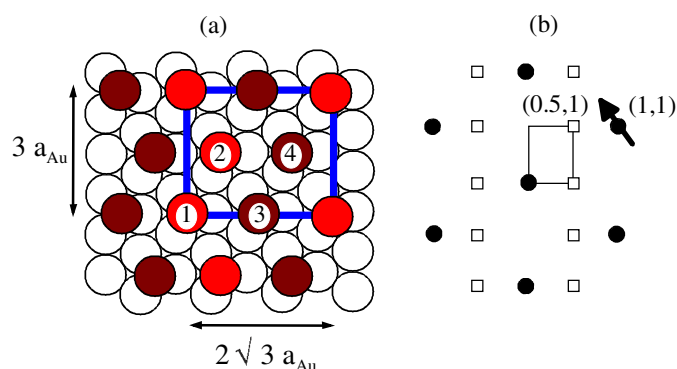
Figure 2. 2D schematic diagram of the real space (a) and the reciprocal space (b) representation of the c(4 × 2) structure of decanethiol on Au(111). Note that the notation of this structure as 'c(4 × 2)' is somewhat unconventional. A more conventional notation would be a rectangular $(2\sqrt{3} \times 3)$ in units of the nearest-neighbour spacing of the substrate, a_{Au}, as indicated in the figure. The diffraction peaks at (1, 1), (2, 2), etc (full circles) correspond to the hexagonal $(\sqrt{3} \times \sqrt{3})$ R30° structure of the SAM, while the peaks at (0.5, 0), (0.5, 1), etc (open squares) are due to the 'c(4 × 2)' superlattice (note that only one rotational domain is shown). The systematic absence of superlattice peaks (with integer h, such as (1, 0), (1, 2), etc) implies that the molecules labelled 1 and 2 (dark circles in (a)) have to be symmetry equivalent as have to be 3 and 4 (shaded circles).

2.1. Thiol-based SAMs

2.1.1. Full-coverage structure of alkanethiols on Au

Long-chain alkanethiols on Au(111). Alkanethiols with chain lengths between C10 and C22 have been thoroughly characterized. The basic structural motif of a full-coverage monolayer on Au(111) is a $(\sqrt{3} \times \sqrt{3})$R30° lattice. This is already expected based on simple packing arguments, which include the tilt angle of the hydrocarbon chains about 30° away from the surface normal [20–22]. However, upon closer inspection a superstructure (traditionally referred to as c(4 × 2), but more appropriately denoted as $(2\sqrt{3} \times 3)$, see figure 2) was discovered [23, 21, 24–26], and the situation is obviously more subtle.

IR data indicated that there are two symmetry-inequivalent molecules per unit cell [20], and it was found that overall the c(4 × 2) unit cell comprises four molecules. The c(4 × 2) superstructure and the two inequivalent molecules imply a break of the hexagonal symmetry. Since a difference in the twist angle of the molecules is insufficient to explain the diffraction intensities of the superlattice reflections, and since the rather flat out-of-plane (q_z) dependence of the diffraction intensities points to localized (atomically thin) structural features being responsible for the superlattice, the implication is that the sulfur headgroup positions deviate from the hexagonal structure [27].

Generally, investigations of a headgroup structure buried underneath long hydrocarbon chains are non-trivial, and most notably scanning probe techniques cannot easily resolve the issue. Nevertheless, some evidence for a non-hexagonal headgroup structure was reported from spectroscopic methods, such as sum frequency generation (SFG) [28], high-resolution electron energy loss spectroscopy (HREELS) [29], and also from x-ray standing waves (XSWs) [30]. For a more detailed discussion and more extensive referencing, see [6].

Short-chain alkanethiols on Au(111). Since *ab initio* calculations are non-trivial for alkanethiols with longer chains, methylthiols and other short-chain thiols on Au(111) have

received a lot of attention. While longer chains with their flexibility and non-negligible chain–chain interactions are essentially a defining feature of SAMs, methylthiols at least supposedly exhibit the same headgroup–substrate interaction. Nevertheless, it should be emphasized that due to the different balance of the interactions (specifically, chain–chain versus headgroup–substrate), it is not possible to extrapolate the results from short-chain thiols to longer-chain thiols.

Danisman *et al* [31] reported not only that the $(\sqrt{3} \times \sqrt{3})$ structure can be observed, but that annealing of the layers leads to a superstructure. Recently, De Renzi *et al* [32] found that the layers actually exhibit a coexistence of the $(\sqrt{3} \times \sqrt{3})$ structure and a (3×4) phase (with the same coverage as the $(3 \times 2\sqrt{3})$ structure). It is important to note that in both studies the annealing was crucial to establish the equilibrium structure.

The binding site of the sulfur atoms was studied using photoelectron diffraction [33]. For layers with the $(\sqrt{3} \times \sqrt{3})$ structure the sulfur atoms were found to adsorb in atop sites. Unfortunately, however, the layers were not annealed, so that a comparison with the above studies is difficult.

Theory.   On the theoretical side, one should distinguish various approaches related to *ab initio* electronic structure calculations on the one hand and simulations with more or less coarse-grained models for the interactions, which usually aim to describe the phase behaviour (the latter are discussed below). We note that Goddard's group and Garrison's group, using force-field-related methods, produced different models for the c(4×2) structures of decanethiol SAMs [34, 35], but these did not resolve the issue.

We try to summarize the various findings briefly, but we should emphasize that for a full account including the limitations of the computational methods the original publications have to be studied. For a more exhaustive list of references, see, e.g., [6, 10, 36].

The *ab initio* work (in most cases based on density functional theory (DFT)) is mostly focusing on the binding configuration of short-chain thiols on Au(111), and the results by different groups are rather inconsistent.

Early work [37] found the hollow site to be most favourable, confirmed, e.g., in [38]. Later, Grönbeck *et al* [39] and Yourdshahyan *et al* [40] reported the fcc hollow site to be most stable. It was also pointed out that there is a difference between fcc and hcp hollow sites, which is not easily detected in calculations based on a limited number of Au atoms used for the substrate [40].

Other groups reported the bridge site or a 'bridgelike' site (e.g., slightly translated toward the hollow site) to be favourable [41–44]. Vargas *et al*, who also found the bridge site to be most stable, studied the coverage dependence of the adsorption energy for different adsorption sites [45]. They suggested that the c(4×2) structure may be explained in terms of inequivalent bridge sites. The coverage dependence of the structure as well as the superstructure was also found in [46]. The study also addresses the problem of competing minima.

We note that recently Fischer *et al* published work on decanethiols on Au(111) (where the long chains were described with classical potentials, which are coupled to quantum description of the headgroup–substrate interaction) and found bridge and bridgelike sites for the sulfurs (resulting in the c(4×2) structure) [47]. Very recently, Franzen addressed the issue of the chain length dependence and concluded that methylthiol is different from the longer-chain thiols, but that ethanethiol would be a reasonable model for these [48].

A very different model was recently investigated by Molina and Hammer [49], involving vacancies on the Au surface. However, this model was ruled out by the experimental data on methylthiols by Kondoh *et al* [33]. We note that it is also inconsistent with the experimental data on decanethiols, specifically the scans of the 'specular rod' (a significant number of Au

vacancies would lead to very different data on the 'specular rod', irrespective of the model used for the thiol structure) [50].

In summary, although a number of experienced groups has tackled the problem, the results for the energetically most favourable structure remain inconsistent. Since the differences between different sites are small, it is understandable that slightly different computational approaches result in different minima. This is also reflected in the early finding that the corrugation of the headgroup–Au(111) potential is rather small [38], which explains why annealing of the films is so effective.

2.1.2. Phase diagram and phase transitions of thiols on Au

Phase diagram. Although the phase diagram is obviously a very fundamental issue, and several groups have studied it, important questions remain unresolved. While it is a consensus that the lowest-coverage ordered phase is the lying-down structure ('striped phase') and that the highest-coverage phase is the standing-up structure (described above), the intermediate-coverage structures are the still subject of discussions.

The natural limit for the lying-down structure (with the alkyl chains lying parallel to the substrate surface) is simply given by the maximum coverage that is possible in this configuration, which in the case of decanethiol is 27% of the full-coverage standing-up structure. For longer chains, this limit is correspondingly lower. We note that on the temperature axis of the phase diagram the lying-down phase region is limited by the melting point at around 100 °C [51].

Importantly, the standing-up phase does not form immediately beyond 27% coverage (assuming a situation near equilibrium), but only above ≈50% (figure 3). Instead, other structures form at intermediate coverage. These are characterized by intermediate tilt angles (around 50°) or chains lying over each other. Since new structures continue to be reported and since the appearance of the structures depends sensitively on preparation conditions (indicating that in some reports non-equilibrium issues are relevant and that the reported 'structures' are not 'phases' in a strict thermodynamic sense), no clear picture has emerged yet, and we shall not pursue this here, but rather refer to [52–56, 51, 6]. Moreover, there are reports of structural changes on long timescales, also for structures which in other work are considered stable [57, 58].

On a general level, the difficulties in establishing a clear-cut picture of the phase diagram and the appearance of multiple structures with apparently similar energetics reflect the degrees of freedom and the competing interactions in this system.

Phase transitions. Not only important details of the phase diagram are open, but also the *character* of the transitions from one phase to another (as a function of temperature as well as coverage). Even pure 2D systems are non-trivial, and indeed the discussion of the transition is still on-going. Moreover, SAMs are not pure 2D systems due to the strong coupling to the substrate and due to their rather '3D nature' with the chains extending into the third dimension. While it should be clear that SAMs are *not* a case of 2D melting, the interesting question is rather how the multiple degrees of freedom express themselves in the phase transition (e.g., multi-step versus one-step melting).

The experimental efforts to shed light on the issue are focused on full-coverage SAMs. However, only a few methods are able to provide more than a 'fingerprint' of the transition, but rather a quantitative measurement of the decay of the order parameter [6].

Early work by Nuzzo *et al* on C22 using IR [20] suggested a continuous decay of the order over a broad temperature range. Surface x-ray diffraction, on the other hand, which determines
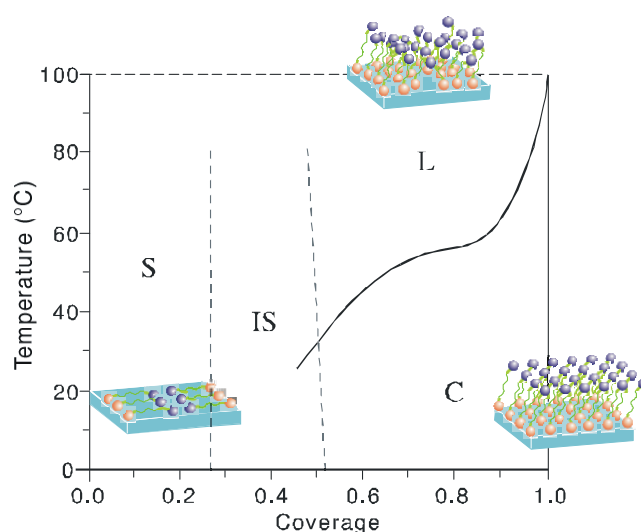
Figure 3. Schematic phase diagram of decanethiol on Au(111) in temperature and coverage space. The different regions and phases are denoted as S (stripes), IS (intermediate structures), C (c(4 × 2)), and L (liquid). The broken lines indicate phase boundaries of the IS, which are not yet fully established. The solid curve between C and L (melting transition) (see [51]) exhibits a sharp rise near full coverage. Note that this is similar to the behaviour found for much simpler systems such as nitrogen on graphite [161].

the order parameter of the crystalline structure directly as the integrated Bragg intensity, found a rather sharp decay at the phase transition of C10 for full coverage (figure 4), whereas for intermediate coverages the transition is broader and at lower temperatures. Remarkably, the precise nature of the transition is still not established[1].

We note that it was recently found that a van der Waals-bound PTCDA capping layer induces a melting point enhancement of 15 K, but leaves the nature of the transition apparently unchanged (figure 4) [59].

Simulations. Given that *ab initio* calculations of long-chain molecules on surfaces are very difficult, various groups used different approaches for describing the interactions and 'coarse-graining' them to some degree. Pioneering work on simulations of SAMs was done by Klein's group [60], followed by many others. For an account of simulation work in the area, we refer to [6, 36, 61, 10, 62, 63] and references therein. While the simulations captured many important aspects (such as tilt structure, multiple phases), the precise shape of the phase diagram (particularly in the intermediate-coverage regime) and the nature of the phase transitions still remain an open issue.

2.1.3. Growth dynamics. In the simplest approximation, the uptake may be expected to follow Langmuir kinetics

$$\frac{\mathrm{d}\theta}{\mathrm{d}t} = (1 - \theta)/\tau, \tag{1}$$

---

[1] We should note that studies of phase transitions of thiols on small gold clusters, as used in NMR, although interesting in their own right, cannot necessarily be compared to results obtained from planar surfaces, *inter alia*, since the relevant domain sizes are limited on clusters and thus the effective defect density is higher (see also [19]).
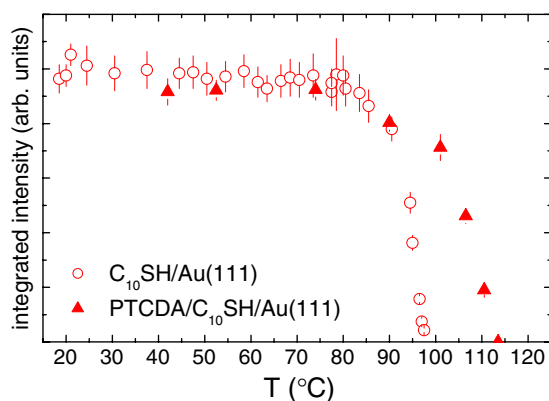
Figure 4. Melting of a full-coverage decanethiol SAM on Au(111) as derived from the integrated intensity of the hexagonal ($\sqrt{3} \times \sqrt{3}$) diffraction peaks measured by GIXD (open symbols). The phase transition at about 100 °C is ~125 K higher than in the bulk ($T_{melt} = -26$ °C). The full symbols refer to the melting of a decanethiol SAM capped by a van der Waals bond PTCDA layer, which increases the melting point by ~15 K compared to the uncapped SAM (see text). From [59].

resulting in $\theta(t) = 1 - \exp(-t/\tau)$ with a time constant τ. However, it was realized that this description is far too crude [6, 51, 64]. First of all, the central assumptions of Langmuir growth (adsorption probability only determined by number of available sites; no lateral interactions) are not fulfilled. More fundamentally, the growth is crossing one or more phase boundaries, as can be seen from figure 3 (constant T and increasing θ). This implies that a higher-coverage phase has to displace a lower-coverage phase [51, 65] and will start with some delay in time and, importantly, will in general experience a different energy landscape and thus a different time constant. In general, τ is expected to be different for every single phase. Indeed, it has been found that, for instance, the standing-up phase grows a factor of $\approx$500 slower than the lying-down phase (for the conditions employed in [51]).

The domain size evolution and nucleation dynamics and their temperature dependence can also be related to the phase diagram, and qualitative differences were found depending on whether or not the growth crosses the region of a very mobile (liquid) phase at intermediate coverages [51]. Other aspects of non-trivial growth behaviour are related to the multiple energy scales (including precursor states), leading to a non-linear dependence of the growth rate on the partial pressure of thiols and involving more elaborate rate equations [6, 66, 67].

After intense research efforts in the 1990s, there is now considerable knowledge about the overall picture and the deviations from simple Langmuir growth. Interestingly, the quantitative data (absolute rates) exhibit significant differences between the various groups [6, 16]. Also, since the growth is connected to the phase diagram, generally, open questions related to phase boundaries necessarily imply that there are open questions for the growth during which these boundaries are crossed. Moreover, the changes brought about by moving further away from equilibrium (in particular when crossing phase boundaries) and how these affect, e.g., nucleation dynamics of emerging phases are not understood.

2.1.4. Other thiol-based systems. So far we have been focusing on alkanethiols on Au(111), but, of course, many other systems have been studied. We shall discuss a few examples.

Other thiols on gold. An interesting question is how the fundamental issues of phase behaviour and growth dynamics are affected by modifications of parts of the molecules.

By using aromatic thiols, the effect of a change of the backbone can be tested. For biphenyl thiols, the same general scenario with a lying-down structure at low coverage and a standing-up structure at high coverage is found [68]. Generally, the phase transition temperatures appear to be higher, which is expected due to the chemically different (and stiffer) backbone. Azzam *et al* found that there are also various structures in the intermediate-coverage regime [69], similar to the alkanethiol case. We note that biphenyls were also used to study odd–even effects (with methylene units inserted between the thiol group and the aromatic part) as a function of the length of the aliphatic chain. The results led to the idea of sp^3 hybridization dominating the bonding scenario for thiols on gold and sp hybridization dominating for thiols on silver [70]. Other phenyl-based SAMs have been discussed, *inter alia*, in [71].

Studies of partially or fully fluorinated SAMs, which may be seen as mimicking Teflon surfaces, are interesting for their wetting properties (see [72] and references therein) as well as for friction and adhesion studies. For structural studies one has to carefully distinguish the various degrees of fluorination and the effect on packing needs (see [6, 72, 73] and references therein).

Dithiols, i.e., compounds with both the headgroup and the endgroup available for linking of, e.g., metal contacts, have been extensively studied in the context of molecular electronics (see below). A central issue is whether one can achieve the ideal scenario of the second thiol group sticking out as an 'anchor' or whether it also binds to the substrate and is much less useable, which strongly depends on the preparation [74].

Thiols on other substrates. Although Au(111) is by far the most popular and probably also the most suitable and easiest-to-handle substrate for thiols, other orientations and other metals have been used as well. The most obvious choices are other coinage metals. For Ag(111), see [75, 10]. On Cu(111), e.g., both short-chain thiols and longer chains were studied [76–79]. It is important to note that, despite the substrates being similar to Au(111) in that they are monovalent, the structures of thiols on Ag(111) and on Cu(111) differ substantially. For thiols on Cu(110), see, e.g., [80]. For a more detailed account and a discussion of metal substrates, see [6].

Recently, Love *et al* studied alkanethiols on Pd [81], which appear superior to SAMs on gold and silver if used as etch resists. Among the differences to the case on gold was the bonding scenario which includes a compound palladium sulfide interphase.

As for semiconductor substrates, generally, the binding of, e.g., thiols on GaAs is more local and thus the mobility of the thiols on the surface is limited, which hampers the evolution of long-range order. Nevertheless, the obvious technological potential of passivating layers or active functional layers on materials used in microelectronics makes them attractive systems to study. Early work was done by Allara and collaborators [82]. For recent work see [83].

Another interesting application of SAMs is the capping of small particles, such as gold nanoparticles, microspheres in colloidal solutions, or semiconductors like CdTe [84]. Here the SAM is used to protect the particles, to act as a spacer preventing coalescence, or, in general, to tailor the interactions with the surrounding medium.

Alkanethiols on liquid metals are interesting systems between SAMs and Langmuir films in that the subphase is liquid, but the thiol group can chemisorb. An important issue is whether the ordering tendency of the molecules dominates or the disorder of the substrate. In an earlier study, no in-plane order was found [85], but after improving the preparation and the control of the coverage, recent results show that an alkanethiol monolayer on mercury can exhibit long-range order, with the molecules tilted or untilted depending on coverage, temperature, and chain length [86].

2.2. Silane-based SAMs

Silane-based SAMs [8] are the second most popular system, but in terms of the relevant mechanisms they differ substantially from thiols on gold. The typical example has a trichlorosilane or similar headgroup, which is irreversibly bound to a hydroxylated surface (e.g., the oxide surface of silicon). In that process the 'sidegroups' (chlorines or other) are split off, and a strongly bound network of the headgroups is generated. This different chemistry of the adsorption process is accompanied by a significant sensitivity to temperature, pH, and water content in solution [6, 16].

From a physical perspective the main differences are the less well defined structure (no long-range order in a crystalline sense; only the tilt angle of the chains displays some degree of order), and the comparatively low mobility of the monolayer molecules on the surface (due to the strong and rather localized binding of the Si–O–Si network). This implies that the structure cannot easily be changed by annealing, but may be considered more 'robust'. For the growth dynamics, a number of different steps (in principle, each with its own timescale), such as adsorption, diffusion, grafting, and cross-linking, have to be taken into consideration [87]. Experimentally, the growth and, in particular, the nucleation dynamics and the associated correlation functions have been thoroughly investigated by the Schwartz group [16].

We note that very recently a new methodology (alternative to the silane strategy) for the preparation of SAMs on the native oxide surface of silicon, based on phosphonates, has been demonstrated [88].

2.3. Other systems

While thiol-and silane-based SAMs are the most popular systems, the general concept of SAMs is, of course, not limited to these. Several different *chemical* routes (headgroup–substrate systems) have been investigated, some involving irradiation with light to initiate the bond-formation. The general *physical* issues related structure and growth are, however, similar to those discussed above. They depend mostly on whether the bonds are either more 'localized' (as for silanes) or more 'delocalized' (i.e., weak corrugation of the potential experienced by the adsorbates, as is the case for thiols on Au(111)), and on the ordering process associated with the chain (flexible versus rigid). For a more detailed list of systems we refer to [6].

3. SAM-based functionalized surfaces and complex systems

In this section, we discuss selected examples for the use of SAMs to functionalize surfaces and as building blocks in more complex heterostructures. The focus is naturally more on the functional properties than on the details of the SAM structure, although it should be emphasized that many applications actually depend crucially on structural details.

3.1. Growth on SAMs

Since the growth behaviour of thin films and coatings depends, *inter alia*, on the surface properties of the substrate (reactivity; surface energy; structure; elastic properties), SAMs can be used to modify the structure of thin films or to anchor coating materials. In this sense, SAMs themselves serve as the 'substrate surface'. We believe that these concepts have a significant potential for materials synthesis.

Several interesting examples for minerals were shown by Aizenberg and collaborators. By choosing the appropriate endgroup of the SAMs and thus the affinity for adsorbates on the SAMs, the growth of crystals such as calcite could be tuned in terms of orientation and shape.

Recently, appropriate patterning of the organic templates was employed to tailor the growth of micropatterned single crystals [89]. Other examples of oxide materials include the anchoring of nanocrystalline ZrO_2 to silicon substrates via silane-based SAMs with sulfonate ($-SO_3H$) endgroups [90].

The concept of surface energy modification can also be employed for the growth of organic crystals. 3,4,9,10-perylenetetracarboxylic dianhydride (PTCDA), a popular dye, on alkanethiol SAMs on Au(111) was studied in [91, 50, 59, 92], and it was found that the PTCDA layer exhibits a well defined epitaxial relation with the underlying SAM. Some groups have compared the growth of pentacene directly on the native oxide layer surface of silicon with growth on a SAM-modified surface. For instance, Shtein *et al* reported the consequences for pentacene-based thin-film transistors on silane-based SAMs [93]. Since in contrast to alkanethiols on Au(111) the silane-based SAMs on siliconoxide do not exhibit long-range order, the issue for growth modification is apparently related to surface energies rather than epitaxial relations. Overlayers of long-chain organic molecules on SAMs were studied by Schwartz *et al* [94].

Another application of the growth of organic materials on SAMs is the alignment of liquid-crystal display materials on SAM-modified surfaces (see, e.g., [95, 96]).

The controlled deposition of metals on SAMs is particularly relevant in the context of molecular electronics (see below). Detailed studies were performed by Allara and collaborators using vapour-phase deposition (see [97] and references therein). The dominating issue is the competition between interpenetration and nucleation of a metal overlayer (for a general discussion of metals on organics, see [98, 99]), and it is found that the results crucially depend on the chemical nature of the SAM endgroups. A route for 'gentle vapour phase deposition' of metals has been reported in [100], which employs 'cooling down' the metal atoms in argon before they strike the surface.

Alternatively, electrochemical methods can be used for metal deposition [101, 102]. While the mechanisms are obviously different, the general issues related to the competition between interpenetration and nucleation are similar.

3.2. Electronic transport through SAMs and molecular electronics

Another attractive concept is the use of functionalized monolayers for molecular electronics. Basic device structures include rectifiers and (more advanced) transistors. The challenges are twofold: one is to design molecules with suitable architecture for the desired device function, and the other is to prepare the monolayer including the contacts such that the resulting structure is sufficiently well defined. Various approaches have been employed. For a review of the background, we refer to [103–105]. A discussion of the difficulties associated with and the limitations of SAM-based field-effect transistors can be found [106, 107].

Some of the limitations are related to contacting problems. One possible approach is the use of an STM tip as one electrode, although the realization in device applications may be non-trivial. For instance, Ashwell and coworkers used an STM tip to contact a molecule comprising donor and acceptor groups linked via an electron bridge (π system), i.e. 'D$-\pi-$A', and have found rectification behaviour [108], as have many others.

Related to this device-oriented work are the rather fundamental studies of electronic transport through individual molecules, for which it is found that comparatively small changes in the endgroup can strongly change the tunnelling characteristics. Pflaum *et al* studied the differences between CH_3- and CF_3-terminated alkanethiols using scanning tunnelling spectroscopy (STS) [73]. Whereas for the regular alkanethiols (CH_3 terminated) the tunnelling current increases steadily with voltage and the shape of the I/V-spectra resembles essentially

those of clean gold (apart from a scaling factor), the CF_3-terminated SAMs exhibit a significant gap. This is apparently induced by the negative 'excess' charge on the endgroup, which may be seen as a barrier for electron tunnelling.

Very popular systems for fundamental studies of electron transport through 'molecular wires' are based on phenylene ethynylene oligomers (using thiol groups for coupling to the electrode). This route has been intensively studied by the groups of Allara, Weiss, and Tour as well as others. One experimental approach is to use a very low concentration of the molecules under study isolated in a matrix of alkanethiols. A finding using STM/STS is that the time evolution of the conductance switching exhibits a different behaviour depending on the ordering quality of the surrounding matrix, which the authors interpret as a result of conformational changes in the molecules (or bundles) rather than electrostatic effects of charge transfer [109]. Very recently, a bond-fluctuation mechanism was proposed for these effects, and the debate appears to be still on-going (see [110] and references therein).

Other groups have used related compounds (i.e., also phenylene–ethynylene based, but different 'side groups') with thiol units at both ends. Reichert *et al* have studied the current through single molecules using a lithographically fabricated mechanically controlled break junction (MCB) [111]. Taylor *et al* have studied the issue using first-principles calculations [112]. Other approaches to contacting the molecule have also been employed. Kushmerick *et al* have used crossed-wire junctions [113], while Rawlett *et al* used phenylene–ethynylene-based dithiols, to the outer thiol group of which a Au nanoparticle was attached, which was then studied using a conducting AFM [114]. The 'mechanochemical' aspects of gold nanowire formation by 'pulling' a single thiol molecule anchored to a stepped gold surface were studied by Krüger *et al* [115, 116].

The role of the anchoring group (S versus Se versus Te) was addressed, e.g., in [117, 118].

Generally, we expect that the area of monolayer or single-molecule-based electronics will thrive further, although the difficulties and limitations should not be ignored [106, 107]. At the same time, SAMs serve as a model system for the investigation of electronic signal transmission through individual molecules.

3.3. SAMs and electrochemistry

In electrochemical applications, surface modification by SAMs is very frequently used. The work until 1996 has been reviewed in [119]. Since the electrochemical properties of the endgroup (and the backbone) can be relatively easily varied, the use of SAMs in electrochemistry continues to be popular.

A very interesting example is phase transitions as a function of the potential. For instance, Schweizer *et al* have reported potential-induced structural transitions for ethanethiol on Au(100) [120], and Vericat *et al* [121] and Byloos *et al* [122] have studied longer alkanethiols on Au(111). Generally, the electrochemical potential offers a broad range of possibilities not only from a chemical, but also from a more physical perspective, since it is an additional control parameter, and more studies of this type may be expected [123].

3.4. Switchable SAMs

An intriguing area is that of 'switchable SAMs'. The idea is to change the SAM properties by an external stimulus such as light or the electrochemical potential (for an account of recent approaches in this area see [124, 125] and references therein).

Ichimura *et al* used a photoisomerizable monolayer to direct the motion of a liquid in contact with the SAM in a spatially varying light intensity, exploiting the fact that the surface energy changes under photoirradiation (*trans*-to-*cis* photoisomerization of azobenzene moieties) [124].
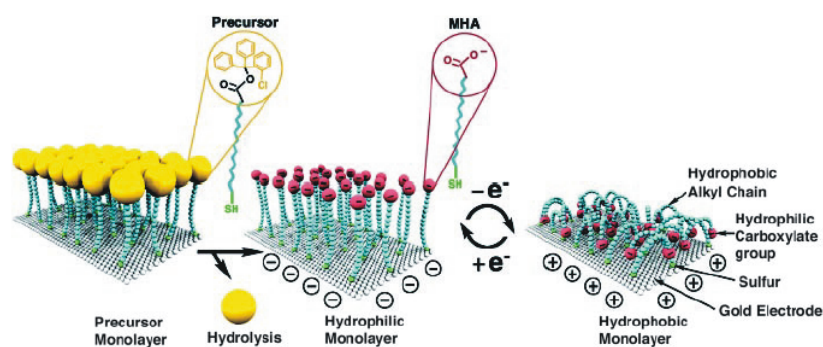
Figure 5. Switchable SAMs. Idealized representation of the transition between straight (hydrophilic) and bent (hydrophobic) molecular conformations (ions and solvent molecules are not shown). After [125].

Recently, Lahann *et al* demonstrated a concept for switchable SAMs under the influence of an electrochemical potential with intentionally created room for conformational changes of the molecules (see figure 5) [125]. First, precursor molecules ((16-mercapto)hexadecanoic acid (2-chlorophenyl)diphenylmethyl ester, MHAE) with a rather bulky headgroup are adsorbed on the surface, resulting in a SAM with a surface number density less than that achievable for the chains. In a second step, the bulky headgroups are split off by hydrolysis, resulting in a low-density, but 'standing-up', layer of (16-mercapto)hexadecanoic acid (MHA). As a result, the endgroups of the MHA molecules are relatively free to move.

The authors performed control experiments with the adsorption of (comparatively short) *n*-butanethiol molecules, indicating that there was apparently no significant MHA cluster formation. We should note that although the second species was actually not used for the switching experiment, it may be an interesting option for future work and one could imagine that suitable compounds may help to stabilize the active layer or to enhance the switching effect.

Electrochemical potentials at rather low values served as external stimuli for the low-density MHA layers. The response (switching) was monitored by SFG as well as by wetting experiments. The SFG data revealed the generation of *gauche* conformations upon switching, implying that the molecules bend their negatively charged end groups towards the positively charged gold surface. The contact angle data confirmed the switching for the (macroscopic) wetting properties.

Interesting areas for future work would be to explore alternative stimuli (besides the electrochemical or light stimulus), to extend the switchable properties (to achieve other types of response), and, probably most rewarding, but also challenging, to switch in the presence of biological material, i.e. also multi-component liquids in contact with the SAM.

3.5. Biorelated applications of SAMs

The possibility to generate a surface with biologically relevant functionalities is certainly one of the most exciting properties of SAMs. A possible scheme is shown in figure 6. The SAM can be terminated with a specific functional group, to which e.g. a receptor can be attached, serving as one part of a lock–key pair to specifically bind a biomolecule of interest. This concept has been pioneered by the Whitesides group. Since then, various other biorelated applications of SAMs have been demonstrated (for a recent update, see, e.g. [126]). Generally, SAMs are popular for biorelated applications for a number of reasons.
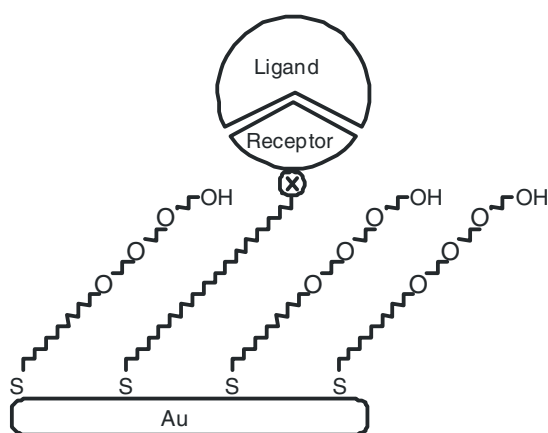
Figure 6. Example for SAM-based bio-interfaces, involving both components for specific adsorption of proteins (following a 'lock–key' mechanism) and components for avoiding unspecific adsorption (using oligo-ethylene-glycol termination).

(1) The relatively straightforward concept of specific binding with the SAM serving as the anchor (see figure 6), and related routes of attaching biomolecules to surfaces.

(2) Biologically 'inert' surfaces (or patches) can be created using OEG- or PEG-terminated SAMs, thus limiting undesired adsorption (see below).

(3) Since cells adhere to surfaces via proteins, the adhesion of proteins to SAMs (and potentially their lateral structure; see below) can be used to manipulate the structure of cells.

(4) Lateral patterning is possible and actually simple, and thus cell growth can be 'shaped'.

(5) Au substrates are compatible with mammalian cells.

(6) SAMs are suitable for electrochemical manipulation.

3.5.1. Ways of attaching proteins to surfaces. In the context of SAMs, several strategies to adsorb proteins on surfaces should be mentioned.

(1) One way is to use the same chemistry as is used for SAM-forming molecules. Recently, Case *et al* reported on the grafting of *de novo* designed metalloproteins incorporating C-terminal thiol groups on gold [127]. In this study, the proteins were 'exchanged' for a small area of pre-assembled octadecanethiol under the action of an AFM tip, resulting in orientational control of the proteins (apparently standing upright). Thiols on gold are an obvious choice, but generally other chemical routes to bind proteins are certainly possible. The 'grafting technique' using an AFM is an additional interesting tool for manipulation in this context [128].

(2) Another way of protein binding is to exploit the concept of lock–key recognition. If the 'lock' is attached via the SAM, then proteins can bind to that endgroup 'lock' via their respective key, thus resulting in specific binding of proteins [129].

(3) Besides controlling the adsorption itself, controlling the molecular *orientation* of the proteins upon adsorption is an important issue. The binding sites on a protein typically occupy only a small fraction of the total surface area of a molecule, so that adsorption on a solid substrate may impair the native binding activity of the protein. It is thus not only important *whether or not* a protein adsorbs, but also *'how'*. One method would be the 'pre-incubation' of the surface with one protein in order to induce orientational order of subsequently adsorbed proteins. For these and related issues, see [130, 131] and references therein. Recent work by Saavedra and coworkers describes efforts to control

the orientational distribution of horse heart cytochrome c by electrostatic interactions (see [132] and references therein).

3.5.2. Oligo-ethylene-terminated SAMs for 'inert' surfaces. As pointed out above, the surfaces which do *not* adsorb proteins (i.e., which are 'inert') can be created using OEG-terminated SAMs [133, 134], either for keeping surfaces generally 'clean' or for avoiding unspecific adsorption, which is a precondition for a meaningful exploitation of specific adsorption. Despite the immense practical importance of this effect, its fundamental understanding is still limited, and several different mechanisms are being discussed.

(1) Israelachvili and Wennerström [135] have discussed the role of hydration and water structure for these interactions. In this context, it is important that the structure of water near interfaces may differ from that in the bulk (see below).
(2) One may also consider the charges which are inevitably associated with proteins and OEG surfaces in contact with water. If the charges are of equal sign and localized by some mechanism, then the proteins would tend to stay at some distance from the surface [136]. The role of electrostatic interactions was studied by Hammond's group using a series of polyamines, which made it possible to control adsorption by varying the pH of the solution and, thus, changing the charge of the polymer [137].
(3) Recently, Kane *et al* [138] related the effect of protein resistance (which is not exclusively found for OEG-terminated SAMs) to the properties of kosmotropes, but the general validity of the hypothesis is yet to be tested.

Recently, Herrwerth *et al* discussed these and other factors very thoroughly, including the importance of water penetrating into the SAM, the packing and defects, and the role of charges [136]. The full picture appears to be rather complex, and it may actually be a combination of different mechanisms.

This complexity is underlined by the observation that *polymeric* ethylene glycol (PEG) renders surfaces protein resistant, but with the underlying mechanisms related to the conformational flexibility of the polymer chains, which are not applicable to densely packed SAMs [139]. In this context, the study of the chain length dependence of OEG SAMs and their protein resistance is interesting.

Because of the importance of PEG and OEG, many groups have studied their various properties. A good overview is found in [136] and references therein. Liedberg's group studied vibrational and conformational properties (see [140] and references therein). Hähner's group, using functionalized AFM tips, addressed the role of salt ions [141]. Schwendel *et al* studied the temperature dependence of the protein resistance and found significant adsorption at low temperatures [142].

3.5.3. Water in contact with SAMs. The interaction of SAM surfaces with water as the ubiquitous medium in biology is particularly important. Recently, the question of the water density near a hydrophobic interface has attracted a lot of attention.

The conclusion appears to be a water layer of reduced density at the interface, but the exact amplitude of the density reduction and the length scale still require investigation [143–145]. For theoretical work, see [146, 147]. We should also mention the effect of 'nanobubbles' near the interface [144] and, of course, usually discussed on macroscopic length scales, wetting control by suitable terminated (or mixed) SAMs [148].

The issue of conformational changes in aqueous electrolytes was studied using amino-amido-thiols in [149].

3.5.4. Other biorelated issues and future challenges.   The utilization of SAMs in the context of biorelated applications certainly extends beyond the question of specific adsorption or repulsion. Chirality is another very important issue. Recently, the Aarhus group reported on chiral recognition in dimerization of cysteine adsorbed on Au(110) [150]. Cysteine (HS–CH$_2$–CH(NH$_2$)–COOH) is the only one of the 20 naturally occurring amino acids that contains a thiol substituent, so that some of the knowledge from thiol-based monolayers can be used.

The concept of SAMs as linkers between biomolecules and metallic electrodes was recently exploited to achieve efficient electrical contact with the electrode (Au) support for a bioelectrocatalytic system. The system was based on the reconstitution of apo-glucose oxidase (apo-GOx) molecules on individual gold-nanoparticle–flavin adenine dinucleotide (FAD) units [151]. The experiment used a dithiol SAM on a gold substrate, with the second thiol group reaching out to bind to a gold (Au$_{55}$) nanoparticle, to which the unit with the enzyme was linked. The reconstituted GOx exceeded the electron transfer features of the native enzyme.

Despite the enormous popularity of SAMs for biorelated applications, there are important challenges. With respect to the fundamental interactions, it appears to be not well understood what really drives the resistance of OEG-SAMs to protein adsorption. Also, the interaction of water with SAM surfaces is an open issue. For applications, still more inert surfaces than OEG-SAMs are desirable. Lastly, a concept that would enable the formation of SAMs on soft substrates (i.e., not Au) would be desirable, since cells on hard substrates are different from their behaviour in their natural environment. With the appropriate 'substrate' (SAM) available, biorelevant species can be adsorbed and immobilized, or their adsorption inhibited. If lateral structuring is included, engineering the cell shape, directing the growth of neurons, and numerous other fascinating applications are possible.

3.6. Lateral structures and patterning

SAMs offer very attractive opportunities for lateral structuring, which is particularly interesting for several of the applications of SAMs discussed above. Various lithography-related techniques have been applied to SAMs [128, 152]. Remarkably, SAMs can act as positive and as negative resists, with 'chemical specificity' in lithography [152].

The most frequently used concept for lateral structures involving SAMs is probably that of micro-contact printing (μCP), which uses a structured stamp to print with an 'ink' of the SAM-forming molecules. This fairly inexpensive methodology has been pioneered by the Whitesides group (see, e.g., [153]). The underlying mechanisms of the printing process and the factors that limit the resolution are related to the wetting properties and the nanofluidics of the system, and they are actually an interesting area in themselves. μCP has been continuously improved, and it has recently led to patterning on the sub-50 nm scale [154].

3.7. Other applications of SAMs

Besides the examples discussed above, there are numerous other applications of SAMs, such as

(1) engineering of wetting properties by appropriate endgroups or mixed SAMs to tune the wetting angle to one between that of the individual constituents,
(2) corrosion inhibition and other protective coatings,
(3) SAMs for adhesion studies,
(4) coating of colloidal particles to tailor the interactions between these and with the solvent,

(5) SAMs for lubrication studies,

(6) SAMs for optical coatings,

(7) SAMs for '*grafted from*' applications (the idea is to 'grow' polymer brushes grafted to a surface by starting a SAM; if the endgroup of the SAM is suitable to start a polymerization reaction, the resulting polymer chain is automatically chemisorbed to the surface via the SAM [155–157]), and

(8) fundamental studies of interactions between spatially fixed molecules (endgroups of SAMs) and atoms or molecules scattered from these [158–160].

4. Conclusions

Twenty years after the discovery of the thiol-on-gold route the area of SAMs is so active and so broad that it is almost impossible to provide a comprehensive review.

The fundamental questions of adsorption, structure, phases, and phase transitions have been thoroughly studied in the past, but several issues actually remain unresolved, probably reflecting the complex competition of multiple interactions and degrees of freedom, giving rise to various structures which are energetically similar.

A large part of present and future work is related to utilizing the various ways to modify and functionalize surfaces by SAMs, with biorelated applications being the most dynamic area. Since SAMs are not so much a specific class of compounds, but rather a very flexible concept with virtually unlimited potential for applications, we expect that the area of SAMs will continue to thrive.

Acknowledgments

References

[1] Gaines G L Jr 1966 *Insoluble Monolayers at Liquid–Gas Interfaces* (New York: Interscience)

[2] Kaganer V M, Möhwald H and Dutta P 1999 *Rev. Mod. Phys.* **71** 779

[3] Ulman A 1991 *An Introduction to Ultrathin Organic Films: from Langmuir–Blodgett to Self-Assembly* (Boston, MA: Academic)

[4] Forrest S R 1997 *Chem. Rev.* **97** 1793

[5] Schreiber F 2004 *Phys. Status Solidi* **201** 1037

[6] Schreiber F 2000 *Prog. Surf. Sci.* **65** 151

[7] Nuzzo R G and Allara D L 1983 *J. Am. Chem. Soc.* **105** 4481

[8] Sagiv J 1980 *J. Am. Chem. Soc.* **102** 92

[9] Swalen J D, Allara D L, Andrade J D, Chandross E A, Garoff S, Israelachvili J, McCarthy T J, Murray R, Pease R F, Rabolt J F, Wynne K J and Yu H 1987 *Langmuir* **3** 932

[10] Ulman A (ed) 1998 *Self-Assembled Monolayers of Thiols* vol 24 *Thin Films* (San Diego, CA: Academic)

[11] Ulman A 1996 *Chem. Rev.* **96** 1533

[12] Whitesides G M and Laibinis P E 1990 *Langmuir* **6** 87

[13] Dubois L H and Nuzzo R G 1992 *Annu. Rev. Phys. Chem.* **43** 437

[14] Poirier G E 1997 *Chem. Rev.* **97** 1117

[15] Zharnikov M and Grunze M 2001 *J. Phys.: Condens. Matter* **13** 11333

[16] Schwartz D K 2001 *Annu. Rev. Phys. Chem.* **52** 107

[17] Pradeep T and Sandhyarani N 2002 *Pure Appl. Chem.* **74** 1593

[18] Ulman A (ed) 2001 *Encyclopedia of Materials: Science and Technology* (Oxford: Elsevier)

[19] Sandhyarani N and Pradeep T 2003 *Int. Rev. Phys. Chem.* **22** 221

[20] Nuzzo R G, Korenic E M and Dubois L H 1990 *J. Chem. Phys.* **93** 767

[21] Fenter P, Eisenberger P and Liang K S 1993 *Phys. Rev. Lett.* **70** 2447 note that the melting temperature (∼70 °C) determined for dodecanethiol was probably for a coverage slightly below 1

[22] Fenter P, Eberhardt A, Liang K S and Eisenberger P 1997 *J. Chem. Phys.* **106** 1600

[23] Camillone N, Chidsey C E D, Liu G-Y and Scoles G 1993 *J. Chem. Phys.* **98** 3503

[24] Poirier G E and Tarlov M J 1994 *Langmuir* **10** 2853

[25] Delamarche E, Michel B, Gerber C, Anselmetti D, Güntherodt H-J, Wolf H and Ringsdorf H 1994 *Langmuir* **10** 2869

[26] Bucher J P, Santesson L and Kern K 1994 *Appl. Phys.* A **59** 135

[27] Fenter P, Eberhardt A and Eisenberger P 1994 *Science* **266** 1216

[28] Yeganeh M S, Dougal S M, Polizzotti R S and Rabinowitz P 1995 *Phys. Rev. Lett.* **74** 1811

[29] Kluth G J, Carraro C and Maboudian R 1999 *Phys. Rev.* B **59** R10449

[30] Fenter P, Schreiber F, Berman L, Scoles G, Eisenberger P and Bedzyk M 1998 *Surf. Sci.* **412/413** 213
Fenter P, Schreiber F, Berman L, Scoles G, Eisenberger P and Bedzyk M 1999 *Surf. Sci.* **425** 138

[31] Danisman M F, Casalis L, Bracco G and Scoles G 2002 *J. Phys. Chem.* **106** 11771

[32] De Renzi V, Marchetto D, Biagi R, del Pennino U, Di Felice R and Selloni A 2004 *J. Phys. Chem.* **108** 16

[33] Kondoh H, Iwasaki M, Shimada T, Amemiya K, Yokoyama T, Ohta T, Shimomura M and Kono S 2003 *Phys. Rev. Lett.* **90** 066102

[34] Gerdy J J and Goodard W A 1996 *J. Am. Chem. Soc.* **118** 3233

[35] Bhatia R and Garrison B J 1997 *Langmuir* **13** 4038

[36] Jiang S 2002 *Mol. Phys.* **100** 2261

[37] Sellers H, Ulman A, Shnidman Y and Eilers J E 1993 *J. Am. Chem. Soc.* **115** 9389

[38] Beardmore K M, Kress J D, Grønbech-Jensen N and Bishop A R 1998 *Chem. Phys. Lett.* **286** 40

[39] Grönbeck H, Curioni A and Andreoni W 2000 *J. Am. Chem. Soc.* **122** 3839

[40] Yourdshahyan Y, Zhang H K and Rappe A M 2001 *Phys. Rev.* B **63** 081405

[41] Hayashi T and Morikawa Y 2001 *J. Chem. Phys.* **114** 7615

[42] Morikawa Y and Hayashi T 2002 *Surf. Sci.* **507–510** 46

[43] Akinaga Y, Nakajima T and Hirao K 2001 *J. Chem. Phys.* **114** 8555

[44] Gottschalck J and Hammer B 2002 *J. Chem. Phys.* **116** 784

[45] Vargas M C, Giannozzi P, Selloni A and Scoles G 2001 *J. Phys. Chem.* B **105** 9509

[46] Yourdshahyan Y and Rappe A M 2002 *J. Chem. Phys.* **117** 825

[47] Fischer D, Curioni A and Andreoni W 2003 *Langmuir* **19** 3567

[48] Franzen S 2003 *Chem. Phys. Lett.* **381** 315

[49] Molina L M and Hammer B 2002 *Chem. Phys. Lett.* **360** 264

[50] Gerstenberg M C, Schreiber F, Leung T Y B, Bracco G, Forrest S R and Scoles G 2000 *Phys. Rev.* B **61** 7678

[51] Schreiber F, Eberhardt A, Leung T Y B, Schwartz P, Wetterer S M, Lavrich D J, Berman L, Fenter P, Eisenberger P and Scoles G 1998 *Phys. Rev.* B **57** 12476

[52] Qian Y, Yang G, Yu J, Jung T A and Liu G-Y 2003 *Langmuir* **19** 6056

[53] Barrena E, Ocal C and Salmeron M 2001 *J. Chem. Phys.* **114** 4210

[54] Barrena E, Palacios-Lidon E, Munuera C, Torrelles X, Ferrer S, Jonas U, Salmeron M and Ocal C 2004 *J. Am. Chem. Soc.* **126** 385

[55] Poirier G E, Fitts W P and White J M 2001 *Langmuir* **17** 1176

[56] Fitts W P, White J M and Poirier G E 2002 *Langmuir* **18** 1561

[57] Barrena E, Ocal C and Salmeron M 1999 *J. Chem. Phys.* **111** 9797

[58] Noh J and Hara M 2002 *Langmuir* **18** 1953

[59] Schreiber F, Gerstenberg M C, Dosch H and Scoles G 2003 *Langmuir* **19** 10004

[60] Hautman J and Klein M L 1989 *J. Chem. Phys.* **91** 4994

[61] Grønbech-Jensen N, Parikh A N, Beardmore K M and Desai R C 2003 *Langmuir* **19** 1474

[62] Pertsin A J and Grunze M 1997 *J. Chem. Phys.* **106** 7343

[63] Bhatia R and Garrison B J 1997 *Langmuir* **13** 765

[64] Dannenberger O, Buck M and Grunze M 1999 *J. Phys. Chem.* B **103** 2202

[65] Poirier G E 1999 *Langmuir* **15** 1167

[66] Eberhardt A, Fenter P and Eisenberger P 1998 *Surf. Sci. Lett.* **397** L285

[67] Schwartz P, Schreiber F, Eisenberger P and Scoles G 1999 *Surf. Sci.* **423** 208

[68] Leung T Y B, Schwartz P V, Scoles G, Schreiber F and Ulman A 2000 *Surf. Sci.* **458** 34

[69] Azzam W, Fuxen C, Birkner A, Rong H-T, Buck M and Wöll C 2003 *Langmuir* **19** 4958

[70] Rong H-T, Frey S, Yang Y-J, Zharnikov M, Buck M, Wühn M, Wöll C and Helmchen G 2001 *Langmuir* **17** 1582

[71] Azzam W, Wehner B I, Fischer R A, Terfort A and Wöll C 2002 *Langmuir* **18** 7766

[72] Alkhairalla B, Boden N, Cheadle E, Evans S D, Henderson J R, Fukushima H, Miyashita S, Schönherr H, Vansco G J, Colorado R Jr, Graupe M, Shmakova O E and Lee T R 2002 *Europhys. Lett.* **59** 410

[73] Pflaum J, Bracco G, Schreiber F, Colorado R Jr, Shmakova O E, Lee T R, Scoles G and Kahn A 2002 *Surf. Sci.* **498** 89

[74] Leung T Y B, Gerstenberg M C, Lavrich D J, Schreiber F, Scoles G and Poirier G 2000 *Langmuir* **16** 549

[75] Fenter P, Eisenberger P, Li J, Camillone N, Bernasek S, Scoles G, Ramanarayanan T A and Liang K S 1991 *Langmuir* **7** 2013 note that the structure reported in this reference was corrected somewhat in [10]

[76] Rieley H, Kendall G K, Chan A, Jones R G, Lüdecke J, Woodruff D P and Cowie B C C 1997 *Surf. Sci.* **392** 143

[77] Rieley H, Kendall G K, Jones R G and Woodruff D P 1999 *Langmuir* **15** 8856

[78] Jackson G J, Woodruff D P, Jones R G, Singh N K, Chan A S Y, Cowie B C C and Formoso V 2000 *Phys. Rev. Lett.* **84** 119

[79] Driver S M and Woodruff D P 2000 *Langmuir* **16** 6693

[80] Kühnle A, Vollmer S, Linderoth T R, Witte G, Wöll C and Besenbacher F 2002 *Langmuir* **18** 5558

[81] Love J C, Wolfe D B, Haasch R, Chabinyc M L, Paul K E, Whitesides G M and Nuzzo R G 2003 *J. Am. Chem. Soc.* **125** 2597

[82] Sheen C W, Shi J-X, Mårtensson J, Parikh A N and Allara D L 1992 *J. Am. Chem. Soc.* **114** 1514

[83] Adlkofer K, Shaporenko A, Zharnikov M, Grunze M, Ulman A and Tanaka M 2003 *J. Phys. Chem.* B **107** 11737

[84] Gaponik N, Talapin D V, Rogach A L, Hoppe K, Shevchenko E V, Kornowski A, Eychmüller A and Weller H 2002 *J. Phys. Chem.* B **106** 7177

[85] Magnussen O M, Ocko B M, Deutsch M, Regan M J, Pershan P S, Berman L E, Abernathy D, Legrand J F and Grübel G 1996 *Nature* **384** 250

[86] Kraack H *et al* 2003 private communication

[87] Bautista R, Hartmann N and Hasselbrink E 2003 *Langmuir* **19** 6590

[88] Hanson E L, Schwartz J, Nickel B, Koch N and Danisman M F 2003 *J. Am. Chem. Soc.* **125** 16074

[89] Aizenberg J, Muller D A, Grazul J L and Hamann D R 2003 *Science* **299** 1205

[90] Ritley K A, Just K-P, Schreiber F, Dosch H, Niesen T P and Aldinger F 2000 *J. Mater. Res.* **15** 2706

[91] Schreiber F, Gerstenberg M C, Edinger B, Toperverg B, Forrest S R, Scoles G and Dosch H 2000 *Physica* B **283** 75

[92] Staub R, Toerker M, Fritz T, Schmitz-Hübsch T, Sellam F and Leo K 2000 *Surf. Sci.* **445** 368

[93] Shtein M, Mapel J, Benziger J B and Forrest S R 2002 *Appl. Phys. Lett.* **81** 268

[94] Schwartz P V, Lavrich D J and Scoles G 2003 *Langmuir* **19** 4969

[95] Gupta V K and Abbott N L 1997 *Science* **276** 1533

[96] Hoogboom J, Behdani M, Elemans J A A W, Devillers M A C, de Gelder R, Rowan A E, Rasing T and Nolte R J M 2003 *Angew. Chem. Int. Edn Engl.* **42** 1812

[97] Walker A V, Tighe T B, Reinard M D, Haynie B C, Allara D L and Winograd N 2003 *Chem. Phys. Lett.* **369** 615

[98] Dürr A C, Schreiber F, Kelsch M, Carstanjen H D, Dosch H and Seeck O H 2003 *J. Appl. Phys.* **93** 5201

[99] Dürr A C, Schreiber F, Kelsch M, Carstanjen H D and Dosch H 2002 *Adv. Mater.* **14** 961

[100] Okazaki N and Sambles J R 2000 *Int. Symp. Organic Molecular Electronics (Nagoya, Japan, May 2000)* pp 66–7 (Extended Abstracts)

[101] Baunach T and Kolb D M 2002 *Anal. Bioanal. Chem.* **373** 743

[102] Epple M, Bittner A M, Kuhnke K, Kern K, Zheng W-Q and Tadjeddine A 2002 *Langmuir* **18** 773

[103] Tour J M 2000 *Acc. Chem. Res.* **33** 791

[104] Joachim C, Gimzewski J K and Aviram A 2000 *Nature* **408** 541

[105] Hänggi P, Ratner M and Yaliraki S (eds) 2002 *Chem. Phys.* **281** 111 (Special issue on transport in molecular wires)

[106] Kagan C R, Afzali A, Martel R, Gignac L M, Solomon P M, Schrott A G and Ek B 2003 *Nano Lett.* **3** 119

[107] Lee J-O, Lientschnig G, Wiertz F, Struijk M, Janssen R A J, Egberink R, Reinhoudt D N, Hadley P and Dekker C 2003 *Nano Lett.* **3** 113

[108] Ashwell G J, Hamilton R and High L R H 2003 *J. Mater. Chem.* **13** 1501

[109] Donhauser Z J, Mantooth B A, Kelly K F, Bumm L A, Monnell J D, Stapleton J J, Price D W Jr, Rawlett A M, Allara D L, Tour J M and Tour P S 2001 *Science* **292** 2303

[110] Ramachandran G K, Hopson T J, Rawlett A M, Nagahara L A, Primak A and Linday S M 2003 *Science* **300** 1413

[111] Reichert J, Ochs R, Beckmann D, Weber H B, Mayor M and Löhneysen H V 2002 *Phys. Rev. Lett.* **88** 176804

[112] Taylor J, Brandbyge M and Stokbro K 2002 *Phys. Rev. Lett.* **89** 138301

[113] Kushmerick J G, Holt D B, Yang J C, Naciri J, Moore M H and Shashidhar R 2002 *Phys. Rev. Lett.* **89** 138301
[114] Rawlett A M, Hopson T J, Nagahara L A and Tsui R K 2002 *Appl. Phys. Lett.* **81** 3043
[115] Krüger D, Fuchs H, Rousseau R, Marx D and Parrinello M 2002 *Phys. Rev. Lett.* **89** 186402
[116] Krüger D, Rousseau R, Fuchs H and Marx D 2003 *Angew. Chem. Int. Edn Engl.* **42** 2251
[117] Patrone L, Palacin S, Bourgoin J P, Lagoute J, Zambelli T and Gauthier S 2002 *Chem. Phys.* **281** 325
[118] Di Ventra M and Lang N D 2001 *Phys. Rev.* B **65** 045402
[119] Finklea H O 1996 *Electroanalytical Chemistry* vol 19, ed A J Bard and I Rubinstein (New York: Dekker)
[120] Schweizer M, Hagenström H and Kolb D M 2001 *Surf. Sci.* **490** L627
[121] Vericat C, Andreasen G, Vela M E, Martin H and Savarezza R C 2001 *J. Chem. Phys.* **115** 6672
[122] Byloos M, Al-Maznai H and Morin M 2001 *J. Phys. Chem.* B **105** 5900
[123] Baunach T, Ivanova V, Scherson D A and Kolb D M 2004 *Langmuir* **20** 2797
[124] Ichimura K, Oh S-K and Nakagawa M 2000 *Science* **288** 1624
[125] Lahann J, Mitragotri S, Tran T-N, Kaido H, Sundaram J, Choi I S, Hoffer S, Somorjai G A and Langer R 2003 *Science* **299** 371
[126] Plant A L, Chen C S, Groves J T and Parikh A N (eds) 2003 *Langmuir* **19** 1449 (Special issue on biomolecular interfaces)
[127] Case M A, McLendon G L, Hu Y, Vanderlick T K and Scoles G 2003 *Nano Lett.* **3** 425
[128] Liu G Y, Xu S and Qian Y 2000 *Acc. Chem. Res.* **33** 457
[129] Sigal G B, Bamdad C, Barberis A, Strominger J and Whitesides G M 1996 *Anal. Chem.* **68** 490
[130] Turková J 1999 *J. Chromatography* B **722** 11
[131] Seeger S, Bierbaum K, Dahint R, Feng C L, Mantar M and Grunze M 1992 *Synthetic Microstructures in Biological Research* ed J M Schnur and M Peckerar (New York: Plenum)
[132] Du Y-Z and Saavedra S S 2003 *Langmuir* **19** 6443
[133] Prime K L and Whitesides G M 1991 *Science* **252** 1164
[134] Harder P, Grunze M, Dahint R, Whitesides G M and Laibinis P E 1998 *J. Phys. Chem.* B **102** 426
[135] Israelachvili J and Wennerstroem H 1996 *Nature* **379** 219
[136] Herrwerth S, Eck W, Reinhardt S and Grunze M 2003 *J. Am. Chem. Soc.* **125** 9359
[137] Clark S L and Hammond P T 2000 *Langmuir* **16** 10206
[138] Kane R S, Deschatelets P and Whitesides G M 2003 *Langmuir* **19** 2388
[139] Jeon S I, Lee J H, Andrade J D and de Gennes P-G 1991 *J. Colloid Interface Sci.* **142** 149
[140] Malysheva L, Klymenko Y, Onipko A, Valiokas R and Liedberg B 2003 *Chem. Phys. Lett.* **370** 451
[141] Dicke C and Hähner G 2002 *J. Am. Chem. Soc.* **124** 12619
[142] Schwendel D, Dahint R, Herrwerth S, Schloerholz M, Eck W and Grunze M 2001 *Langmuir* **17** 5717
[143] Schwendel D, Hayashi T, Dahint R, Pertsin A, Grunze M, Steitz R and Schreiber F 2003 *Langmuir* **19** 2284
[144] Steitz R, Gutberlet T, Hauss T, Klösgen B, Krastev R, Schemmel S, Simonsen A C and Findenegg G H 2001 *Langmuir* **19** 2409
[145] Jensen T R, Østergaard Jensen M, Reitzel N, Balashev K, Peters G H, Kjaer K and Bjørnholm T 2003 *Phys. Rev. Lett.* **90** 086101
[146] Lum K, Chandler D and Weeks J D 1999 *J. Phys. Chem.* B **103** 4570
[147] Pertsin A, Hayashi T and Grunze M 2002 *J. Phys. Chem.* B **106** 12274
[148] Bain C D and Whitesides G M 1989 *Angew. Chem. Int. Edn Engl.* **28** 506
[149] Bittner A M, Epple M, Kuhnke K, Houriet R, Heusler A, Vogel H, Seitsonen A P and Kern K 2003 *J. Electroanal. Chem.* **550/551** 113
[150] Kühnle A, Linderoth T R, Hammer B and Besenbacher F 2002 *Nature* **415** 891
[151] Xiao Y, Patolsky F, Katz E, Hainfeld J F and Willner I 2003 *Science* **299** 1877
[152] Felgenhauer T, Yan C, Geyer W, Rong H-T, Gölzhäuser A and Buck M 2001 *Appl. Phys. Lett.* **79** 3323
[153] Xia Y and Whitesides G M 1998 *Annu. Rev. Mater. Sci.* **28** 153
[154] Li H-W, Muir B V O, Fichet G and Huck W T S 2003 *Langmuir* **19** 1963
[155] Jordan R and Ulman A 1998 *J. Am. Chem. Soc.* **120** 243
[156] Jordan R, Ulman A, Kang J F, Rafailovich M H and Sokolov J 1999 *J. Am. Chem. Soc.* **121** 1016
[157] 2003 *Chem. Eng. News* **81** 41 (Overview article)
[158] Evans C, Pradeep T, Shen J and Cooks R G 1999 *Rapid Commun. Mass Spectrom.* **13** 172
[159] Wolf K V, Cole D A and Bernasek S L 2001 *Langmuir* **17** 8254
[160] Bracco G and Scoles G 2003 *J. Chem. Phys.* **119** 6277
[161] Kuchta B and Etters R D 1996 *Phys. Rev.* B **54** 12057