

Thiol-based Self-assembled Monolayers: Formation and Organization

Self-assembled monolayers (SAMs) form by the spontaneous adsorption of amphiphilic adsorbates onto an appropriate substrate (see Fig. 1). The initial driving force for the assembly is the chemical affinity between the adsorbates and the substrate. Examples of adsorbate–substrate pairs commonly used to generate SAMs include: (i) carboxylic acids on aluminum oxide or silver, (ii) alcohols, amines, and isonitriles on platinum, (iii) alkylsilane derivatives on hydroxylated surfaces, (iv) dialkyl sulfides and dialkyl disulfides on gold, and (v) alkanethiols on metals such as gold, silver, and copper, and nonmetals such as GaAs, InP, and indium–tin oxide (ITO, Ulman 1991). In recent years, much research on SAMs has focused on the alkanethiol-based systems, due largely to their unique combination of attractive features (Ulman 1996). First, these SAMs are easy to generate from either solution or the gas phase. Second, they are densely packed and precisely oriented. Third, the thickness and the surface properties of the films can be easily adjusted using standard organic synthetic methods. Although a variety of substrates have been used to generate alkanethiol-based SAMs, gold has received particular attention due to its chemical inertness, which permits reproducibly well-formed SAMs. As a result, SAMs of alkanethiols on gold are the most thoroughly studied monolayer system and have become the standard by which other organic films are compared (Ulman 1996, Schreiber 2000, see *Thiol-based Self-assembled Monolayers, Structure of*).

This article will discuss the formation and organization of thiol-based SAMs, with an emphasis on the alkanethiol–gold system. The first section will provide background information concerning self-assembly and self-assembled films. The second section will discuss basic monolayer preparation techniques. The third section will summarize the substrates commonly used to form SAMs. The fourth section will provide a

brief overview of the types of thiol-based adsorbates used to form SAMs. The final section will focus on the chemistry of the thiol–substrate interface and will discuss adsorption reactions and energetics, the structure of fully formed monolayer films, and adsorption kinetics.

1. Background on Self-assembled Films

Self-assembly is a phenomenon in which a number of independent molecules suspended in an isotropic state come together to form an ordered aggregate. This phenomenon is ubiquitous in nature, as seen in the formation of micelles by surfactants, bilayers by lipids, or biological cells by living organisms. Self-assembled films are formed when molecules organize themselves in a 2D arrangement on the surface of a substrate as shown in Fig. 1.

An early description of self-assembled films was reported by Benjamin Franklin in the eighteenth century. He observed that a spoonful of oil spontaneously spread to cover the surface of a pond. The amphiphilic oil molecules had reorganized themselves to maximize the contact of their polar functionalities with the polar water molecules of the pond. In the nineteenth century, Agnes Pockles and Lord Rayleigh performed the first fundamental experiments on oil–water interfaces, which established methods for reproducibly generating these films and provided evidence of a layered structure that was only one molecule thick. Despite these early efforts, oil-on-water films are now named after the twentieth century scientist Irving Langmuir, because he was the first to provide a modern understanding of their structure (e.g., orientation of the adsorbates) at the molecular level. Later, Katherine Blodgett and Langmuir showed that the adsorbates in a Langmuir monolayer could be transferred to a solid support to generate a physisorbed monolayer. The development of these

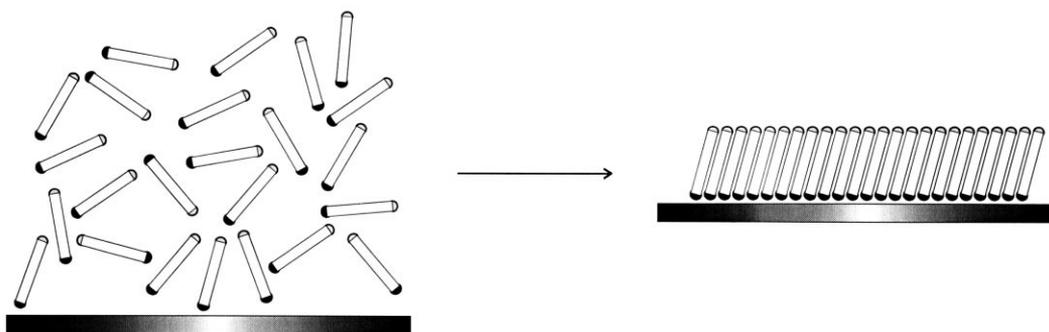


Figure 1
Self-assembly of amphiphilic adsorbates onto a solid surface.

Langmuir–Blodgett (LB) films was significant because it demonstrated that the interfacial properties of solid surfaces could be influenced by merely adsorbing a thin organic film (see *Langmuir–Blodgett Films, Formation and Structure of*).

Zisman conducted the first systematic studies of SAMs on solid substrates. These films were generated by dipping a metal or metal oxide surface into a solution of adsorbates, such as alkylamines or carboxylic acids. The resulting films were unwet by the solvent used for monolayer generation (i.e., they were autophobic) and exhibited interfacial properties similar to those of LB films. Zisman showed that the driving forces involved in self-assembly were ligating chemical interactions between the polar functional groups of the adsorbates and the metal or metal oxide atoms. This feature differentiated the latter “self-assembled” films from LB films, where the adsorbate–substrate interactions were primarily of a physical nature. Zisman also provided evidence that chemical interactions gave rise to a preferred orientation of the adsorbates with their polar groups adsorbed to the solid substrate and their nonpolar alkyl chains directed away from the substrate to expose a surface composed predominantly of methyl groups. The surface formed by these terminal groups possessed low interfacial free energy and, therefore, repelled the solvent molecules, giving rise to the observed autophobicity. In the 1950s and 1960s, Zisman continued to study the properties of these SAMs. One of the most significant results of his studies was the observation that the interfacial properties (e.g., wetting and friction) of the films could be controlled by changing the chemical identity of the terminal functional groups. For example, the interfacial free energy of a SAM could be lowered by substituting the terminal methyl groups for trifluoromethyl groups. Zisman exploited this result to study the relationship between the interfacial energetics of organic thin films and their chemical and physical structures. Notably, SAMs were used as model systems to estimate the interfacial free energies of solids. However, the films generated by Zisman suffered from a number of drawbacks that limited their use in technological applications. Namely, the energies of adsorption between the adsorbates and substrates were low (5–15 kcal mol⁻¹), which afforded only modest stabilities. Also, obtaining films of reproducible quality was complicated due to difficulties in obtaining pristine metal or metal oxide surfaces.

In 1983, Nuzzo and Allara reported the formation of oriented monolayers of dialkyldisulfide adsorbates (RSSR) on the surface of gold. Furthermore, the interfacial free energy of the monolayers were observed to range from low values to high values depending on the chemical nature of the terminal functional groups in the R chains. This work sparked interest in exploring SAM systems based on sulfur–metal interactions. Soon afterwards, it was discovered that other organosulfur compounds such as alkane-

thiols and alkyl sulfides also co-ordinated to the surfaces of metals such as gold, silver, and copper to afford SAMs (Porter *et al.* 1987, Bain *et al.* 1989, Laibinis *et al.* 1991). Of these systems, most of the recent work on SAMs has focused on the alkanethiol–gold system for at least four reasons (Laibinis *et al.* 1998). (i) In metal systems such as silver and copper, the formation of a native oxide layer or the adsorption of other contaminants often competes with the adsorption of the organosulfur compounds; however, gold is relatively inert and forms no stable oxide under ambient conditions. (ii) Both sulfur and gold are considered “soft” chemical entities according to “hard–soft” acid/base theory; thus, the interaction between sulfur and gold atoms is favorable and highly specific. This specificity ensures that sulfur will be preferentially adsorbed over other “hard” chemical moieties (e.g., –OH, –OR) that may be present in the adsorbate. As a result, thiol-based adsorbates can be designed to expose “hard” terminal groups—similar to those present in organic or biological systems—at the surface of the monolayer. (iii) The backbones of alkanethiol adsorbates consist of alkyl chains that, in densely packed films, possess thermodynamically favored trans-extended conformations. Within the monolayer, attractive van der Waals interactions between the chains serve to stabilize the film structure. (iv) The simple chemical structure of alkanethiols renders them ideal for modification using organic synthesis.

In considering the formation and organization of the variety of thiol-based SAMs, it is useful to divide the structure of the adsorbate molecule into three parts (Fig. 2). The first part consists of the thiol moiety (–SH) and is referred to as the *headgroup*. The chemisorption of this headgroup to the substrate is the most energetic and most important process in monolayer formation. The second part consists of the alkyl chain and is referred to as the *methylene spacer*. Van der Waals interactions between chains, while energetically weaker than chemisorption, still provide a significant driving force for adsorbate organization. The third part consists of the terminal functional group, which is referred to as the *tailgroup*. In normal alkanethiol-based SAMs, these groups are methyl moieties. The tailgroups are exposed at the outermost surface of the monolayers, and thus exert the most direct influence on the interfacial properties of the films. For this reason, chemical modification of the tailgroup is an active field of research (Laibinis *et al.* 1998, Graupe *et al.* 1999). In addition, modification of the tailgroups can alter the structure of the interface by introducing additional steric or electrostatic interactions.

2. Basic Monolayer Preparation Techniques

Thiol-based SAMs have historically been prepared from either of two methods: growth from solution or

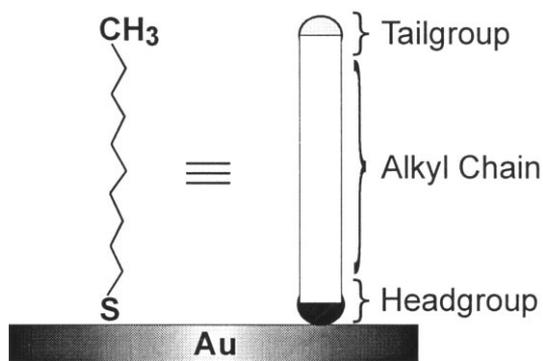


Figure 2

Depiction of an alkanethiol adsorbate on the surface of gold, depicting the tailgroup, alkyl chain, and headgroup.

growth from the gas phase. Differences between these two methods in the kinetics of monolayer formation will be discussed in Sect. 5. In both cases, the highest possible purity of both the adsorbates and the substrates is desired.

2.1 Growth from Solution

The initial studies of thiol-based SAMs employed deposition from solution (Porter *et al.* 1987, Bain *et al.* 1989). In this method, a dilute solution of the thiol (1 μM to 1 mM) dissolved in an appropriate solvent is prepared. Ethanol has been the solvent of choice because it readily dissolves most thiols and can be affordably obtained in pure form. In the next step, a clean substrate is immersed into the thiol-containing solution. An incubation period of 24h is typically allowed to permit monolayer formation to equilibrate, although kinetics experiments have shown that full monolayer formation actually occurs on a substantially shorter time scale (see Sect. 5). After this period, the monolayer-coated substrate is removed from solution and rinsed with an appropriate solvent to remove any adsorbate molecules that might be physisorbed to the surface of the monolayer. The rinsing solvent is typically the same as that used to generate the films, but other solvents in which the adsorbate molecules are soluble can also be used. The monolayer is then dried under a stream of ultra-pure inert gas (typically nitrogen or argon) and is stored until used.

Bain *et al.* (1989) studied the effect of the solvent on the formation of hexadecanethiol monolayers on gold. The following solvents were used: hexadecane, carbon tetrachloride, toluene, acetonitrile, cyclooctane, ethanol, tetrahydrofuran (THF), and dimethylformamide (DMF). While the solvent appeared, in general, to exert no substantial influence on the characteristics (e.g., wettabilities and thicknesses) of the fully formed

films, the monolayers adsorbed from hexadecane exhibited reproducibly higher wettabilities. To explain this observation, the authors proposed that the molecules of the nonpolar solvent had incorporated themselves into the monolayer structure during formation, thereby raising the interfacial free energy. The proposed intercalation was perhaps facilitated by the linear structure of the solvent molecules and the strong intermolecular interactions (van der Waals attractions) between the solvent molecules and the alkyl chains of the adsorbates. Therefore, the ideal solvent for SAM formation should not only dissolve the adsorbate molecules, but also resist intercalation into the monolayer. While the studies by Bain *et al.* (1989) also showed that dipping the substrate into neat adsorbate could generate a monolayer, the volume of adsorbate needed to cover the surface area of a typical substrate (e.g., $\geq 1\text{ cm}^2$) is considerably larger than that used to generate a dilute solution. This feature becomes important when dealing with chemically modified adsorbates that may be available only in milligram quantities.

2.2 Growth from the Gas Phase

In recent years, many modern surface science techniques have been adapted to study organic thin films (Schreiber 2000). Because of the nature of these techniques (i.e., the use of radiation and particle beams), the experiments are typically conducted in an ultra high vacuum (UHV) chamber. Adsorbate molecules are typically placed in a container that is connected to the chamber through a dosage valve, which is used to control the flow of adsorbate vapor into the chamber. The container may require warming to introduce adsorbates that possess low vapor pressures. The primary advantage of this method over growth from solution is the inherent cleanliness of the UHV system. Also, since UHV chambers are typically equipped with a variety of complementary analytical instruments, several distinct types of analyses can be conducted without requiring transfer from one instrument to another.

3. Substrates Commonly Used to Form SAMs

As previously discussed, thiol-based SAMs can be generated by adsorption onto a range of metals and nonmetals. Studies of SAMs on metallic substrates typically utilize evaporated films or single crystals. Since gold is the most commonly used metallic substrate, details of its preparation are included below.

3.1 Preparation of Evaporated Gold Surfaces

Since gold resists oxidation, it can be handled without requiring exhaustive precautions. Furthermore, com-

mon airborne contaminants that might adsorb on the gold surface tend to interact weakly such that thiols readily displace them to generate well-formed SAMs. In the literature, the most widely used surfaces for SAM formation are evaporated films of gold (~ 1000 – 2000 \AA) deposited onto flat surfaces of silicon wafers, glass, or mica. In the foremost case, polished and cleaned silicon wafers are mounted in a vacuum chamber that is evacuated to pressures below 1×10^{-5} torr. Given that the strength of the adhesive interaction between gold and the native oxide layer of silicon is weak (due to the poor oxophilicity of gold), a thin layer (100 \AA) of chromium or titanium is first evaporated onto the silicon surface to promote the adhesion of gold. Evaporation of the gold is usually accomplished by passing an electrical current through a tungsten filament that supports the gold. The current resistively heats the filament until the gold atoms vaporize and deposit onto the primed surface of the wafers. The rate of metal deposition is typically held between 0.1 – 1.0 nm s^{-1} . This procedure allows for the generation of pure gold surfaces over large areas ($> 100 \text{ cm}^2$). The resultant gold surfaces are polycrystalline and exhibit a predominantly (111) texture with crystal grains $\sim 50 \text{ nm}$ in diameter (Laibinis *et al.* 1998).

The polycrystalline domains of evaporated gold surfaces on silicon are sufficiently large for characterization with analytical techniques (e.g., IR reflection absorption spectroscopy (IRRAS) and x-ray photoelectron spectroscopy (XPS)) that average over macroscopic spatial areas (e.g., 1 mm^2); however, the investigation of monolayer structure at the molecular scale with scanning probe microscopies (SPM) requires domains that are atomically flat over larger areas (e.g., $> 100 \times 100 \text{ nm}^2$). Mica is a layered inorganic material that can be cleaved into sheets that possess atomically flat domains. If gold is evaporated under vacuum onto heated (~ 250 – 450°C) mica sheets, the gold atoms form epitaxial layers having domains that appear as flat terraces with diameters of typically $0.2 \mu\text{m}$. Imaging of the atomic structure by SPM reveals a hexagonal arrangement of gold atoms that correspond to Au(111) (Laibinis *et al.* 1998).

3.2 Preparation of Single Crystal Surfaces

SAMs manipulated under UHV conditions are most commonly formed on the surfaces of metallic single crystals. The crystals are cleaned by sputtering the surface with an ion beam (e.g., Ar^+). The crystals are then annealed to allow for reconstruction of the surface. The sputtering and annealing is repeated until contaminants are removed as indicated by *in situ* analysis (e.g., Auger spectroscopy). The samples can then be dosed with the appropriate thiol. This method has been successfully employed for gold, silver, and copper (Schreiber 2000).

3.3 Other Substrates

Polycrystalline substrates other than gold might require alternative methods of preparation (Ulman 1996). While silver and copper substrates can also be prepared by evaporation, special precautions must be used to prevent surface contamination and/or oxidation before monolayer formation. These evaporations are conducted in an analogous manner to that used for gold, but an inert gas (argon or nitrogen) must be used to backfill the vacuum chamber and to surround the substrates while transferring them to the monolayer solutions. Platinum substrates have been generated by evaporation onto quartz slides, and thin mercury films have been generated by electrochemical deposition onto appropriate substrates. Oxide-free vacuum-melted iron substrates have been prepared by electrochemical etching in perchloric acid, followed by immediate functionalization with the neat alkanethiol. Semiconductors such as GaAs or InP can be obtained as polished wafers from the manufacturers, cleaned with chemical etchants, and then immersed in thiol solutions. ITO substrates can be prepared by evaporating a film onto the surface of glass slides.

4. Thiol-based Adsorbates Used to Form SAMs

A wide variety of thiol-based adsorbates have been used to generate SAMs. Each portion of the adsorbate (tail, spacer, and head) has been targeted for chemical modification in attempts to alter or control specific film properties. For example, the identity of the tailgroup has been varied to produce films with low, intermediate, and high interfacial free energies. Additionally, reactive functionalities have been used as tailgroups to facilitate covalent attachment of other chemical species to the SAMs. Tailgroup modifications have also been employed to tune the surface properties of SAMs used in technological applications. Two of the most common examples of these modifications involve the incorporation of biochemical functionalities and electroactive moieties. Polymeric functional groups have also been incorporated into both the tails and the spacers of adsorbates in attempts to generate 2D networks within the films. In contrast to the commonly used alkyl moieties, much activity has focused on the incorporation of aromatic functional groups in the films. Recently, efforts have sought to enhance film stability by employing chelating headgroups (Shon *et al.* 1999). The properties of SAMs formed from a number of these and related adsorbates are the subject of a comprehensive review (Laibinis *et al.* 1998).

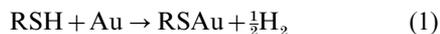
The most commonly used thiol-based adsorbates are the normal alkanethiols ($\text{CH}_3(\text{CH}_2)_n\text{SH}$). Moreover, SAMs generated from these compounds are the most well characterized and widely studied (Bain *et al.* 1989, Ulman 1991). Hence, the characteristics of these

films are used as convenient starting points to interpret the results of film formation from more structurally complex adsorbates. The compounds are commercially available in high purity for a variety of chain lengths ($n = 0-15, 17$), and can, therefore, be readily obtained for monolayer formation and study.

5. Chemistry of the Thiol-Substrate Interface

Although it is generally accepted that thiol-based self-assembly on gold occurs through chemisorption, the exact nature and mechanism of this reaction is not well understood. The reaction has been proposed to occur via oxidative addition of the alkanethiol RS-H bond to the metallic gold substrate Au⁰ (Ulman 1996). However, it is unknown whether the mechanism occurs through an ionic, radical, or other pathway. There is evidence by XPS, vibrational spectroscopy, mass spectrometry, and electrochemical techniques that the thiols adsorb to form an Au-S bond in which the sulfur exists as a thiolate (i.e., reduced). The exact fate of the thiol hydrogen atoms upon adsorption, however, remains an issue of continued conjecture. The most commonly proposed hypothesis is that the hydrogen atoms react to generate H₂. Additionally, it has been proposed that the hydrogen atoms react with the gold surface to form metal hydrides. Furthermore, in the presence of oxidants, the hydrogen atoms might react to form water or hydrogen peroxide. Nevertheless, these proposals are purely speculative, since, to our knowledge, no investigation has obtained incontrovertible evidence for any of these products.

To estimate the energetics of adsorption, it is convenient to consider the following simplified reaction:



Here we assume that the following steps comprise adsorption: (i) cleavage of the RS-H bond, (ii) formation of the RS-Au bond, and (iii) loss of the H as H₂. The bond dissociation energies for these processes are as follows: RS-H (87 kcal mol⁻¹), RS-Au (40 kcal mol⁻¹), and H-H (104 kcal mol⁻¹). From these values, the overall free energy of the reaction (ΔG_{ads}) is calculated to be -5 kcal mol^{-1} , suggesting an exothermic adsorption process. Karpovich *et al.* proposed that the modest value of ΔG_{ads} indicates a balance between enthalpic and entropic contributions to adsorption. The enthalpy of adsorption (ΔH_{ads}) for an alkanethiol on gold ($-28 \text{ kcal mol}^{-1}$) was assumed to be similar to that of a dialkyl disulfide on gold determined by Nuzzo *et al.* Using this value and the free energy of adsorption, the entropy of adsorption is estimated to be large and negative. These researchers verified these estimates by measuring the kinetics of octadecanethiol adsorption on gold with a quartz crystal microbalance (QCM). The observed rate of adsorption (k_{obs}) was measured for a variety of

different temperatures and monolayer solution concentrations in *n*-hexane. From these data, ΔG_{ads} was calculated to be $\sim 5.5 \text{ kcal mol}^{-1}$ when the temperature ranged from 288 K to 303 K. The data also permitted the calculation of the equilibrium constant for adsorption (K_{eq}) over this range. From the temperature dependence of K_{eq} , ΔH_{ads} was calculated to be $-20 \text{ kcal mol}^{-1}$. These values are related to the entropy of adsorption (ΔS_{ads}) by the following equation:

$$\Delta G_{\text{ads}} = \Delta H_{\text{ads}} - T\Delta S_{\text{ads}} \quad (2)$$

The temperature dependence of ΔG_{ads} was used to determine a value of ΔS_{ads} equal to $-48 \text{ cal mol}^{-1} \text{ K}^{-1}$. The relatively large magnitude and negative value of ΔS_{ads} apparently reflects the great degree of ordering that occurs as the alkanethiols change from randomly distributed orientations in solution to highly oriented 2D crystalline lattices on the surface.

5.1 Structure of Fully Formed Monolayers

The structure of SAMs of alkanethiols on gold can be viewed from two useful perspectives. The first perspective is the top view, which presents the 2D structure of the adsorbates projected onto the surface of the substrates (Fig. 3(a)). Important structural features from this view are the quality of the packing of the adsorbates (i.e., ordered or disordered), the symmetry of the packing structure, the registry of the adsorbates with the underlying substrate, and the lattice spacing between the adsorbates. The second perspective is the side view (Fig. 3(b)), which presents the structure of the adsorbates extending above the surface. Important structural features from this view are the extension and conformation of the alkyl chains and the tilt and twist angles of the alkyl chains with respect to the surface normal. Early diffraction studies of the monolayer structure with low energy atomic diffraction (LEAD) revealed that the adsorbates were close packed in a hexagonal arrangement that exhibited a $(\sqrt{3} \times \sqrt{3})\text{R}30^\circ$ registry with the underlying Au(111) surface (Chidsey *et al.* 1989). Given the 2.9 Å nearest-neighbor spacing of Au(111), this structure corresponds to a lattice spacing of $\sim 5 \text{ Å}$ between adsorbates. Accordingly, the sulfur headgroups were proposed to sit in the three-fold hollow sites of the Au(111) lattice. Additional studies by LEAD, grazing incidence x-ray diffraction (GIXD), and scanning tunneling microscopy (STM) have revealed the existence of a $c(4 \times 2)$ superlattice of the $(\sqrt{3} \times \sqrt{3})\text{R}30^\circ$ overlayer structure (Ulman 1998, Schreiber 2000). The presence of the superlattice has been attributed to the existence of distinct orientations (e.g., twist angles) of the alkyl chains within a unit cell and/or the inequivalency of binding sites for the sulfur headgroups (e.g., deviation from the $(\sqrt{3} \times \sqrt{3})\text{R}30^\circ$ binding structure or formation of disulfides on the surface). Studies by IRRAS have revealed that the alkyl chains

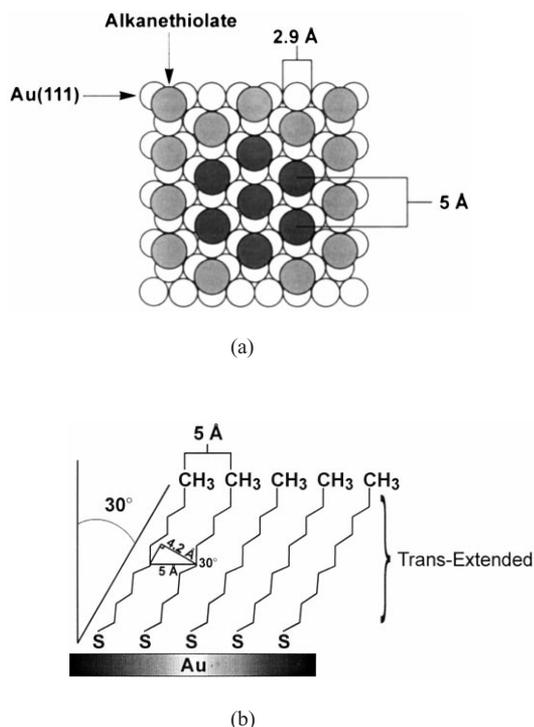


Figure 3

Structure of SAMs of alkanethiols on Au(111) from two different perspectives. (a) Top view, where the open circles represent gold atoms in a hexagonal close-packed arrangement, and the shaded circles represent alkanethiolate adsorbates (the darker shaded circles highlight the hexagonal ($\sqrt{3} \times \sqrt{3}$)R30° overlayer structure), and (b) side view, where the adsorbates are packed 5 Å apart with their alkyl chains tilted 30° from the surface normal in a trans-extended conformation.

are predominately trans-extended and tilt $\sim 30^\circ$ from the surface normal to maintain a stabilizing interchain van der Waals distance of 4.2 Å. SAMs generated from both solution-phase and gas-phase adsorption exhibit structural features that are indistinguishable. More details of the structure of fully formed monolayers can be found in *Thiol-based Self-assembled Monolayers, Structure of*.

5.2 Kinetics of Monolayer Formation

Bain *et al.* (1989) first investigated the kinetics of thiol-based monolayer adsorption onto gold. The wettabilities and thicknesses of SAMs generated from ethanolic solutions having concentrations ranging from 1 μM to 1 mM were monitored by contact angle goniometry and optical ellipsometry, respectively. The results indicated that two distinct kinetic regimes characterized film growth. The first regime took place within the range of seconds to a few minutes, during

which time 80–90% of total film formation occurred (fast regime). The second regime took place within the range of minutes to several hours, during which the contact angles and thicknesses reached limiting values (slow regime). Since these initial studies were performed, the growth kinetics of SAMs have also been investigated by a variety of other techniques (Karpovich *et al.* 1998, Schreiber 2000). These include, IRRAS, QCM, STM, XPS, second harmonic generation (SHG), near edge x-ray absorption fine structure (NEXAFS), surface plasmon resonance spectroscopy (SPR), atomic force microscopy (AFM), thermal desorption spectroscopy (TDS), and radio-isotopic labeling. Collectively, these analyses support the aforementioned two-regime model of adsorption; however, the exact details of the process (e.g., regime duration) vary among the reports. The variations plausibly arise from differences in the experimental conditions used. These include: (i) the purity, concentrations, and/or chain lengths of the adsorbates, (ii) the nature of the adsorption medium (e.g., gas-phase versus solution-phase or polar-solvents versus non-polar solvents), (iii) the cleanliness and quality of the gold substrate, and (iv) the temporal sensitivity of the analysis. Furthermore, while the final film structure of SAMs generated from either solution-phase or gas-phase adsorption might be equivalent, the stepwise processes by which they are formed and the sensitivity of these processes to external control (e.g., temperature, concentration) can differ substantially (see also *Thiol-based Self-assembled Monolayers, Structure of, Self-assembled Monolayers by Evaporation*).

5.3 Kinetics of Solution-phase Monolayer Formation

For deposition from solution, the purity of the solution and the cleanliness of the substrate are primary concerns. The presence of contaminants, either adsorbed from solution or pre-adsorbed onto the substrate, can influence the adsorption kinetics since the thiol adsorbates must ultimately displace the contaminants to chemisorb. Indeed, the presence of contaminants has been reported to induce a delay in monolayer formation (Schreiber 2000). Furthermore, the quality (e.g., size of the (111) terraces, the roughness, and the density of defects) of the gold surface can also influence the growth process. Care must also be taken to ensure that the concentration of adsorbates in solution is precisely controlled, particularly when comparing the kinetics of formation from different solutions. Most studies have found that the rate of monolayer formation increases with increasing concentration of thiol in solution. In fact, at millimolar concentrations and above, monolayer formation occurs too rapidly for monitoring by most of the aforementioned techniques. For this reason, kinetic studies are most commonly conducted using micromolar concentrations.

Assuming that the contributions of the aforementioned factors are controlled or at least understood, a general picture of the growth process can be developed. The initial fast regime is proposed to involve adsorption of the thiol headgroup to the surface of gold. The general consensus is that this step occurs on a much shorter time scale than processes in the second slow regime, and can thus be considered separately. For probing monolayer kinetics, it is, therefore, favorable to differentiate between events occurring during the fast regime and those occurring during the slow regime. In the past, many *ex situ* analyses (e.g., ellipsometry, contact angle goniometry) were unable to deconvolute these two regimes. For example, attempts to probe the fast regime by using short immersion times (seconds) can be hampered because film growth might still proceed under “slow-regime” conditions while the sample is being transferred and prepared for analysis. Recently, *in situ* analyses (e.g., QCM, SHG, SPR) that can selectively probe film growth as it occurs in the short time domain have been developed (Schreiber 2000).

(a) *Kinetics in the fast regime.* At least four different models have been proposed to rationalize the kinetics of adsorption in the fast regime. A brief review of the techniques and models used to probe monolayer kinetics thus far is provided in Dannenberger *et al.* 1999. The most commonly proposed kinetic model for this first regime is that of Langmuir adsorption (see Eqn. (3)), where the growth rate (k_L) from a solution of concentration (c) is proportional to the fraction of available adsorption sites (θ , which is equivalent to the surface coverage). In the Langmuir adsorption model,

$$\theta = 1 - \exp(-ck_L t) \quad (3)$$

all adsorption sites act independently (i.e., there are no interactions between adjacent sites), and there is no multilayer formation. Modifications of this model are needed if, in fact, the adsorbates do interact with one another during film growth or if the rate of adsorption is influenced by factors other than the number of available sites, such as diffusion through the solution or through the partially formed monolayer.

Peterlinz and Georgiadis followed monolayer formation by SPR (Peterlinz and Georgiadis 1996). In their studies, a diffusion-limited Langmuir model (DL) was proposed in which the time dependence of Eqn. (3) was adjusted to give:

$$\theta = 1 - \exp(-ck_{DL} t^{0.5}) \quad (4)$$

Their data were also reasonably fit by a nondiffusion-limited second order Langmuir model (SO), which follows:

$$\theta = 1 - (1 + ck_{SO} t)^{-1} \quad (5)$$

Schlenoff *et al.* (1995) used radioisotopic labeling to monitor the kinetics of formation and suggested that the first regime followed a purely diffusion-controlled model rather than a Langmuir model. Their studies proposed a rate constant (k_{DC}) that depended on a diffusion constant (D) and the number of molecules per unit area at full surface coverage (B_{ML}) as shown in Eqn. (6):

$$\theta = ck_{DC} t^{0.5} \quad (6)$$

Dannenberger *et al.* (1999) probed the kinetics of monolayer formation with SHG, which measures changes in the optical response of the gold substrate as the thiols chemisorb (i.e., formation of the S–Au bond). Their data were fit with each of the four previously mentioned kinetic models to determine which would yield the best match. The simple Langmuir model (Eqn. (3)) provided the most consistent representation of the results. There were, however, slight deficiencies in the fit with the Langmuir model. In particular, the model predicted rates that were faster than those experimentally measured at low coverages and rates that were slower than those experimentally measured at high coverages. Refinements of the Langmuir model (based on a modified Kisliuk model) were proposed to correct these discrepancies. In the Langmuir model, chemisorption occurs at a rate k_L after the solvated thiol moves toward the surface and displaces any adsorbed solvent molecules (or contaminants) to expose an adsorption site. The probability that a thiol chemisorbs (or “sticks”) through this process can be represented by a sticking coefficient $S_D(\theta)$. The modified model suggested an additional pathway for chemisorption, where a solvated thiol might strike islands of thiolates (already chemisorbed through the former pathway). The probability that a thiol impinges on one of these islands is given by the sticking coefficient $S_E(\theta)$. From this intermediate state, the thiol can then either be incorporated into the island to form a thiolate at a rate k_{EC} or desorb from the surface of the island at a rate k_{ES} . This analysis yields the following relation for the time-dependent change in surface coverage:

$$\frac{d\theta}{dt} = c \left[\frac{S_D(1-\theta) + S_E\theta(k_{EC}(1-\theta))}{k_{EC} + k_{ES}(1-\theta)} \right] \quad (7)$$

By assuming that desorption of the thiol back into solution occurs much more quickly than incorporation into an island of thiolates, Eqn. (7) can be simplified to:

$$\frac{d\theta}{dt} = ck_L(1-\theta)(1+k_E\theta) \quad (8)$$

In this equation, $k_E\theta$ represents the deviation from the

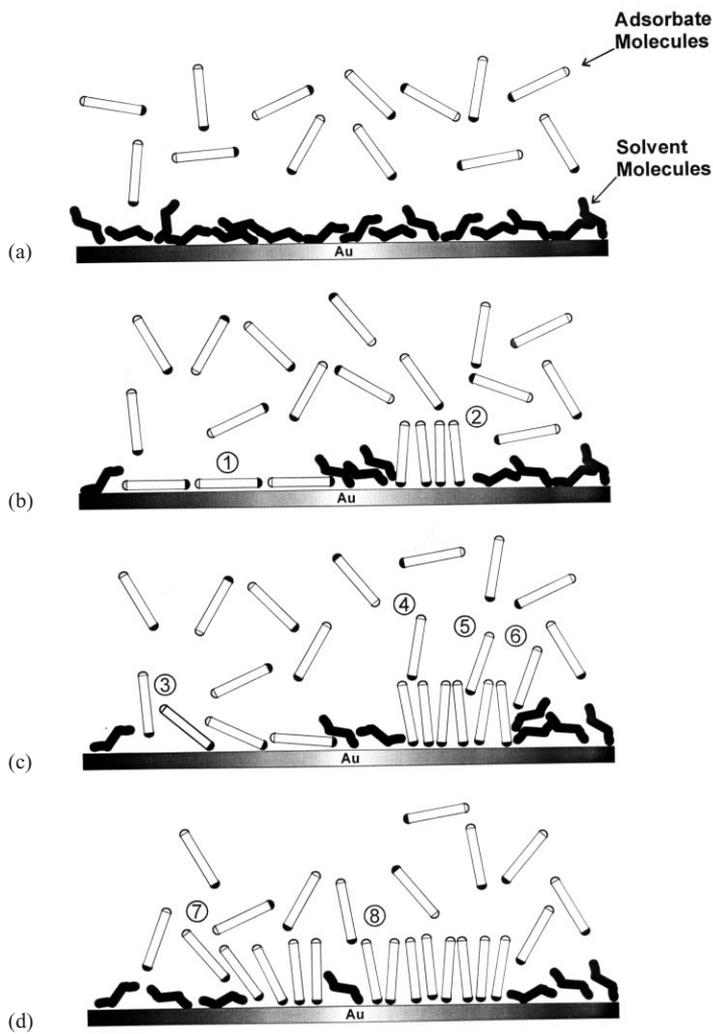


Figure 4

Illustration of the adsorption processes occurring in the fast regime. (a) The adsorbate molecules in solution approach the gold substrate, which is coated with a layer of physisorbed solvent molecules (Note: the solvent molecules surrounding the adsorbate molecules have been omitted for clarity.) (b) The adsorbate molecules displace the solvent molecules to form either lying-down domains (1) or upright domains (2). (c) Additional adsorbate molecules incorporate into the lying-down domains and initiate a transition to an upright domain (3). Alternatively, adsorbate molecules can impinge on the surface (4), within the boundaries (5), or at the boundaries (6) of upright domains and incorporate into the domains. (d) The upright domains formed from either the lying-down phase (7) or direct adsorption (8) continue to grow until maximum coverage is attained.

Langmuir model due to the influence of the islands of thiolates. Equation (8) can be rearranged to give:

$$\theta = \frac{\exp[(1+k_E)ck_L t - 1]}{\exp[(1+k_E)ck_L t + k_E]} \quad (9)$$

This modified model provided a better fit of the data and suggested that thiols already present on the surface (in the form of islands of thiolates) contributed to

monolayer formation in the fast regime by promoting the adsorption of additional thiols. This analysis also rationalizes the observed deviation from the Langmuir model since the adsorption of thiols is influenced by adsorbates at adjacent sites.

The growth of monolayers via the formation of thiolate islands has been observed by both STM (Yamada and Uosaki 1998) and AFM (Xu *et al.* 1999). During the earliest stages of film growth, a low coverage “striped” phase was observed. In this phase,

the thiol molecules are adsorbed onto the gold substrate with their alkyl chains lying parallel to the surface. With continued immersion, a phase transition occurs in which the thiol molecules presumably “stand up” and form islands of thiolates with their alkyl chains oriented nearly perpendicular to the surface. These islands continue to grow by incorporating thiols (either at the boundaries of or within the islands) and eventually coalesce to form larger domains. It has been proposed that the striped phase initially consists of physisorbed thiols that, at some later stage of the growth process, chemisorb to the gold surface. The SHG results by Dannenberger *et al.* (1999) reveal that chemisorption from micromolar solution occurs within the first few seconds. Consequently, the lifetime of the physisorbed stage must be short compared to that of the chemisorbed stage. This suggestion is supported by the requirement of sub-micromolar concentrations ($0.3\ \mu\text{M}$) to observe the striped phases by STM in studies of decanethiol SAM formation conducted by Yamada and Uosaki. As the concentration was increased to $3\ \mu\text{M}$, no striped phases were observed, and the surfaces were covered with islands consisting of upright thiolates. These results were attributed to either direct formation of islands upon adsorption (i.e., without forming an intermediate striped phase) or an increased rate of transition from the striped phase to islands that is too fast to be detected by STM. Nevertheless, both the SHG and the SPM experiments demonstrated that micromolar solutions yield surfaces that are fully covered by thiolate islands within a few minutes. The adsorption processes occurring in the fast regime are summarized in Fig. 4.

Yamada and Uosaki (1998) also observed a short-lived etching process that occurred prior to film formation in which pits formed on the surface of gold upon exposure to the thiol solutions. This etching process was proposed to occur by chemisorption of a thiol adsorbate followed by immediate desorption of a gold–thiolate complex. Evidence for this process has also been obtained by the detection of gold by atomic absorption spectroscopy in monolayer solutions after SAM formation (Dannenberger *et al.* 1999); however, at the concentrations commonly used for monolayer formation, film formation is more likely to occur than this process.

(b) *Kinetics in the slow regime.* During the slower second regime, structural annealing of the alkyl chains of the adsorbed thiolates has been proposed to occur. This proposal has been supported independently by SPR, IRRAS, and NEXAFS studies. Himmelhaus *et al.* (2000) investigated the kinetics of this second regime by monitoring the formation of docosanethiol monolayers on gold from micromolar ethanolic solutions with IR–visible sum frequency generation

spectroscopy (SFG). This technique can follow the conformational ordering of the C–H stretching modes as a function of time, and, therefore, provides information on the evolving structure of the alkyl chains during film growth. The first state observed in this study corresponded to the adsorption process that occurs during the fast regime, and was characterized by alkyl chains possessing a high number of gauche defects. In the slow regime, an ordering of the alkyl chains occurs with a rate that is 3–4 times slower than that of the first process. During this ordering process, the alkyl chains straighten from highly kinked conformations to predominately trans-extended conformations, thereby increasing the film thickness (see Fig. 5). A subsequent process, which occurs at a rate that is at least 35 times slower than the chain straightening process, was also observed. This final process was attributed to the reorientation of the terminal methyl groups. The data indicated that the incorporation of the last 10–20% of adsorbates induces a final ordering of the monolayer from the substrate to the outermost portion of the film, which gives rise to the limiting values of film thickness and wettability observed for fully formed SAMs.

(c) *Effect of control factors.* The kinetics of monolayer formation described above can also be influenced by a number of factors, such as the concentration of solution (*vide supra*), the total chain length of the thiols, the nature of the solvent, and the temperature. Bain *et al.* (1989) compared the kinetics of adsorption of decanethiol and octadecanethiol from 1 mM ethanolic solutions onto gold and found that the films generated from the shorter adsorbate reached limiting values of both hexadecane and water contact angles more slowly. These results were attributed to two effects: (i) the presence of poorly packed alkyl chains and/or film defects plausibly influenced the contact angles of the decanethiol SAM more than those of the octadecanethiol SAM, and (ii) the selective incorporation of hexadecane molecules into the thicker SAM increased the contact angles by improving the packing of the alkyl chains. Note that these studies were performed at relatively high concentrations of thiol (1 mM), which accelerates the kinetics; furthermore, these *ex situ* analyses plausibly reflect processes that have occurred over both the fast and slow kinetic regimes.

Both Dannenberger *et al.* (1999) and Peterlinz and Georgiadis (1996) explored the kinetics in the fast regime as a function of alkanethiol chain length. Both groups found that the rate of the initial adsorption process decreased as the chain length of the adsorbates increased. These results were rationalized in terms of the mobility of adsorbate molecules, which increases with decreasing chain length. Molecules with higher mobilities are more capable of impinging on an

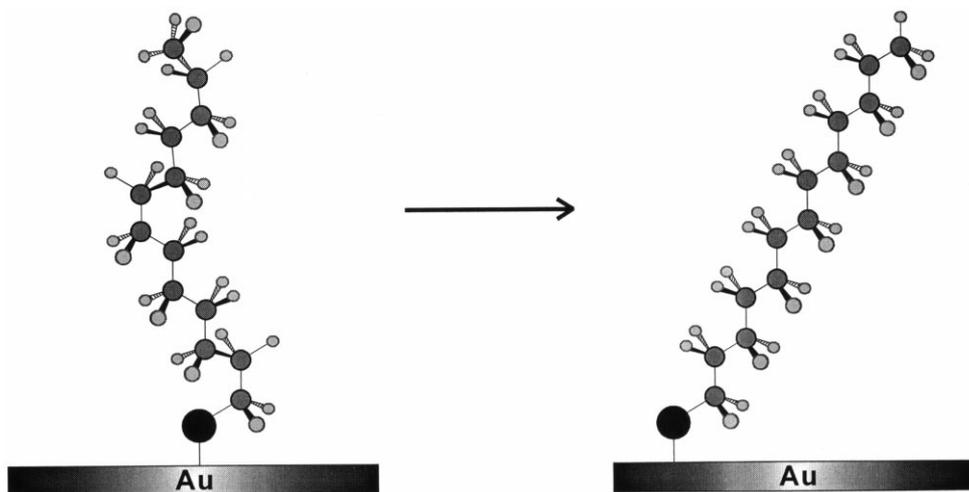


Figure 5

Chain straightening from a kinked conformation to a *trans*-extended conformation.

adsorption site that has become exposed (through displacement of the solvent or separation of thiolates within or at the boundaries of an island) and can consequently be adsorbed at a higher rate. In contrast, Xu *et al.* (1998) reported that the longer docosanethiol formed complete SAMs more readily than the shorter octadecanethiol as determined by *in situ* AFM experiments. The difference in rate was related to the stronger van der Waals interactions between longer adsorbates, which would promote the incorporation of additional thiols into preformed islands. Undoubtedly, both the mobility of the adsorbates and the strength of interchain interactions play significant roles in the growth process (*vide supra*). The discrepancies in the data are most likely due to differences in the temporal resolution of the techniques used. For example, longer chain lengths can plausibly lead to faster chain annealing during the slow regime, since the increased number of interchain interactions would promote a more rapid conformational ordering of the alkyl chains to the *trans*-extended state.

Shon and Lee (2000) have compared the kinetics of monolayer formation for 2,2-dipentadecylpropane-1,3-dithiol (*d*-C17) and 2-pentadecylpropane-1,3-dithiol (*m*-C17) with those of *n*-heptadecanethiol (*n*-C17) (see Fig. 6) using ellipsometry, contact angle goniometry, and polarization modulation IRRAS. These studies revealed that the rate of film formation in the slow regime was substantially slower for *d*-C17 than for *m*-C17 and *n*-C17. The data were rationalized in terms of the relative ability of the molecules to become incorporated into thiolate islands by diffusion through partially formed domains. Since the molecular size of *d*-C17 is approximately twice that of both *m*-C17 and *n*-C17, the former molecule plausibly experiences a greater steric barrier to diffusion, which

decreases the rate of adsorption in the slow regime. These results further highlight the influence of intermolecular interactions between adsorbates upon the rates of monolayer formation.

Varying the nature of the solvent can also influence monolayer kinetics via solubility, polarity, mobility, and solute-solvent steric effects (Ulman 1991, Schreiber 2000). Due to the diversity of factors, comparisons between solvents of widely differing chemical and/or physical structures can be intractable. Dannenberger *et al.* simplified the comparison by studying the adsorption of docosanethiol from 2 μ M solutions in *n*-alkanes of increasing chain length (C6, C12, and C16). As the chain length of the solvent increased, the rate of the initial adsorption step (fast regime) decreased. These results were interpreted to reflect the influence of adsorbed solvent molecules on the kinetics of adsorption. During the earliest stages of immersion, the solvent molecules presumably physisorb to the gold surface through van der Waals interactions. Given that the number of van der Waals interactions for *n*-alkanes increases with the total chain length, longer solvent molecules would plausibly interact more strongly with the gold surface than would shorter solvent molecules. A stronger interaction translates into a lower probability for displacement from the surface by impinging thiols, which would in turn decrease the rate of adsorption.

Few experiments have probed the influence of temperature on the kinetics of monolayer formation from solution (Schreiber 2000). Karpovich *et al.* (1998) measured the rate of the initial adsorption step (fast regime) from 288 K to 303 K for 0.2 mM octadecanethiol solutions in hexane. The rate was independent of temperature over the investigated range. These data challenged claims that the adsorption of

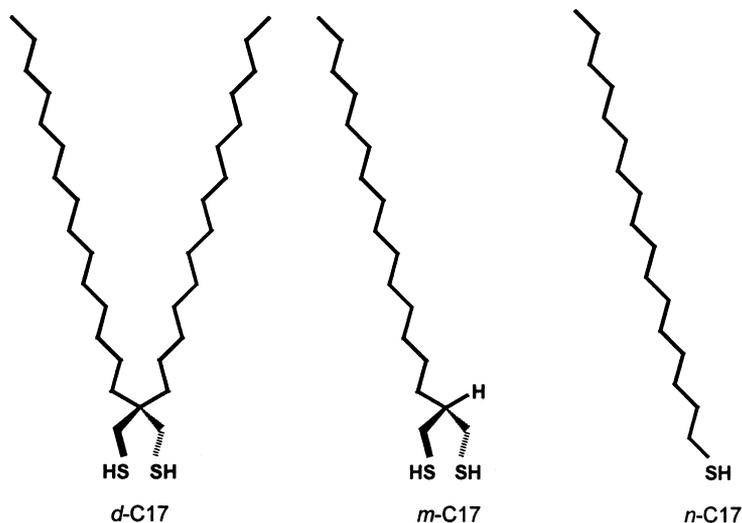


Figure 6

Structure of the alkanethiols used in the kinetics studies conducted by Shon and Lee (2000): (*d*-C17) 2,2-dipentadecylpropane-1,3-dithiol, (*m*-C17) 2-pentadecylpropane-1,3-dithiol, and (*n*-C17) *n*-heptadecanethiol.

normal alkanethiols was diffusion-limited, since the rate of a diffusion-limited reaction should exhibit a linear dependence on temperature.

(*d*) *Kinetics of gas-phase monolayer formation.* Analysis of the kinetics of monolayer formation in the gas phase is a more straightforward process than that of the solution phase, since (i) solvent interactions can be excluded, (ii) the cleanliness of the surface can be precisely controlled and monitored, and (iii) a variety of *in situ* techniques can be used, such as GIXD, LEAD, STM, TDS, XPS, low-energy electron diffraction (LEED), Auger photoelectron spectroscopy (AES), x-ray standing wave spectroscopy (XSW), and helium atom reflectometry (HAR). Schreiber *et al.* (1998) studied the gas-phase deposition of decanethiol on Au(111) with XPS, LEAD, and GIXD. The coverage of the gold surface was monitored via the XPS-measured sulfur 1s photoelectron yield as a function of the exposure to thiol vapor. The data suggested that full coverage proceeded through a two-step process, involving a rapid initial step followed by a step that was ~ 500 times slower. These processes could be fit with a Langmuir model. Experiments using LEAD revealed that the first step involves the formation of a striped phase in which the adsorbate molecules lie down on the substrate with their alkyl chains parallel to the surface in a $p(11 \times \sqrt{3})$ configuration with respect to the hexagonal structure of Au(111). The coverage at this stage was estimated to be 0.27 of a fully formed monolayer (where 1 monolayer = 4.6×10^{-14} molcm $^{-2}$ for decanethiol in a hexagonal $(\sqrt{3} \times \sqrt{3})R30^\circ$ arrange-

ment on Au(111)). Between coverages of 0.27 to 0.47 monolayers, no ordered phases were observed. This intermediate stage was proposed to represent a transition between the striped phase and the final phase. During this transition, it is possible for many metastable structural states to exist. Analysis by GIXD revealed that the final step involves the formation of a standing-up phase in which the alkyl chains of the adsorbate molecules are oriented nearly perpendicular to the surface. The molecules are adsorbed in a $c(4 \times 2)$ superlattice of the hexagonal $(\sqrt{3} \times \sqrt{3})R30^\circ$ overlayer structure on gold. These phases nucleate and grow until a full monolayer is formed. This phase was detected for coverages between 0.47 and 1.0 monolayer. Overall, these results suggest that film growth in the gas phase evolves through a series of transitions between discrete phases. Further evidence for this mechanism has been provided through the STM investigations of decanethiol adsorption on gold performed by Poirier (1999). In this work, both the striped phase and the standing-up phase were imaged at the anticipated coverages. Additionally, a number of phases were observed for the intermediate states. The observation of ordered phases during the intermediate state by STM but not by the aforementioned diffraction techniques can be rationalized by the fact that STM is sensitive to local structure, while the diffraction techniques probe over larger areas. Therefore, short-range order can plausibly exist during the intermediate range in the absence of any long-range order.

(*e*) *Solution-phase versus gas-phase deposition.* The major difference between solution-phase and gas-

phase monolayer formation arises from the presence of solvent molecules (Karpovich *et al.* 1998, Schreiber 2000). Generally, the energy of adsorption (i.e., the difference in energy of the free molecule and the adsorbed molecule) for the solution-phase will be less than that of the gas-phase as a result of the attractive interactions with the solvent. In addition, the kinetics of film growth can also be influenced by the presence of solvent. For example, the formation and persistence of the striped-phase during solution-phase formation can be limited due to the presence of solvent. Prior to thiol adsorption, a layer of physisorbed solvent molecules exists on the gold surface. These solvent molecules must be displaced in order for the thiol to adsorb. The number of displaced solvent molecules required for the thiol to adsorb in a lying-down orientation is greater than that needed to adsorb in a standing-up orientation. Furthermore, the energy gained upon replacing a physisorbed solvent molecule with a physisorbed lying-down thiol molecule can be smaller than the energy gained upon replacement with an upright chemisorbed thiolate. Consequently, the formation of upright thiolate domains directly from solution might, in some cases, be favored over formation from striped-phase precursors. In the event that a lying-down phase does persist, however, solvent molecules can facilitate the transition to an upright phase by replacing the alkyl chain-surface interactions with surface-solvent and alkyl chain-solvent interactions. In contrast, the gold substrates that are used under UHV conditions during gas-phase monolayer formation are free of any adsorbates (i.e., solvent or contaminants). Consequently, the vaporized thiol molecules need not displace any species to adsorb, and thus might initially maximize the number of attractive interactions with the surface by lying down. These differences are representative of the factors that give rise to the unique mechanisms observed for each method of adsorption (*vide supra*), despite the fact that equivalent final monolayer structures are produced.

6. Concluding Remarks

The topics addressed above represent only the most fundamental investigations of thiol-based SAM formation and organization. At present, research involving SAMs spans a vast range of academic disciplines and technological applications.

See also: Self-assembled Monolayer Films: Electrochemical Properties; Self-assembled Monolayer Films: Electro-optic Applications; Self-assembled Monolayer Films: Microcontact Printing; Polyelectrolyte Self-assembled Multilayer Films: Molecular Beaker Epitaxy; Thiol-based Self-assembled Monolayers, Structure of; Self-assembled

Monolayers by Evaporation

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