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REVIEW PAPER

NANO-ENGINEERING OF MOLECULAR FILMS BY SELF-ASSEMBLY AND LANGMUIR-BLODGETT TECHNIQUES

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The availability of sophisticated and ultra-sensitive analytical tools and the maturity of organic synthesis have opened new possibilities for fabrication of molecular materials designed at the nanometer scale. Presently, the most promising and widely investigated methodologies are the self-assembly and Langmuir-Blodgett procedures. The former relies on the strong, preferential affinity of specific functional groups to solid surfaces, whereas the latter involves transfer of pre-formed monolayers at the air-water interface onto solid substrates. These techniques and their recent applications are reviewed.

Keywords: monolayers; ultrathin films; self-assembly technique; Langmuir-Blodgett technique

INTRODUCTION

Smaller and smaller devices are not hard to notice, which are present in many of today's important electronic devices: computers, television sets, cameras, and many others. This may be attributed largely to developments in very large scale integrated (VLSI) circuit technology. The semiconductor industry provided us with miniscule electronic chips whose circuitry is in the micrometer-size domain. Hence, the term "microelectronics." However, there is now a global trend to fabricate even smaller devices which led to such buzzwords as "nanotechnology" [1,2] and "nanodevices;" the prefix "nano" refers to dimensions within the nanometer scale (a thousandth of a micrometer). A major contribution to nanotechnology by chemists would perhaps be motivated by the wide ability of modern-day organic chemists to synthesize many specialty molecules. This contribution partly leads to revitalized interest in molecular assemblies, because they yield new materials with potential technological uses in optoelectronic devices, sensors, electro-optical switches, information storage, adhesion, lubrication, and a slew of "smart" materials [3]. The applications of organic-based assemblies span the entire fields of science and engineering which is evident in the large number of and wide-ranging areas in scientific reports involving this type of materials [1-6].

Considerable research activity is devoted in the area of molecular films, which thus finds many reviews on the subject [4-6]. Molecular materials are attractive for various technological applications because mature organic synthesis can incorporate special functionality into the molecules for desired physico-chemical properties. However, the structure and organization of the ensemble of molecules that make up the material also affect the bulk properties. Thus, material design entails a two-fold challenge: synthesis of the specialty molecules; and, suitable fabrication of the material.

Here, we make a cursory review of fabrication of molecular films with thicknesses ranging from a few Angstroms (e.g., a monomolecular layer) to hundreds of nanometer (several monolayers). The popular methodologies to date can be classified as either a self-assembly or Langmuir-Blodgett technique; these techniques will be reviewed along with recent examples from literature. This paper is by no means an extensive review but aims only to familiarize the reader with these methodologies; more extensive reviews on the subjects are cited [4-6].

SELF-ASSEMBLED MONOLAYERS (SAMs)

Definitions. The term "self-assembly" has been applied to many systems and situations, e.g., in the spontaneous

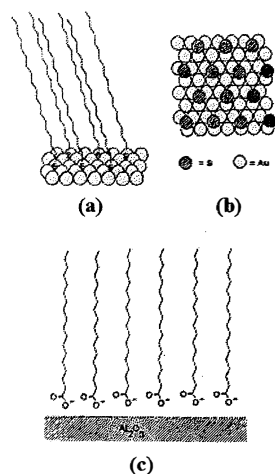


Fig. 1. Schematic diagrams for SAMs: (a) long-chain alkanethiol on gold with (b) the packing orientation of the sulfur head group on a Au (111) surface; and, (c) fatty acid on a metal oxide surface

adsorption of molecules from solution onto solid surfaces (SAMs), in the spontaneous organization of amphiphiles at the air-water interface to form Langmuir monolayers [7] or in solution forming molecular aggregates such as micelles and membranes [8], in the spontaneous organization or rearrangement of biomolecules [9-10], and in the spontaneous formation of new phases such as liquid crystals [11] or microdomains in polymers [12]. Apparently, the term is generic for many processes, molecular or not, that is both spontaneous and leads to a net organization different from the original state. Thermodynamically, a definition of self-assembly will relate it to any process of formation or state of organization of molecules defined by an overall decrease in the free energy ($\Delta G < 0$) and a concomitant decrease in the entropy of the ensemble ($\Delta S < 0$) [8]. This definition applies to the *self-assembly* technique for making molecular films. It is differentiated from the Langmuir-Blodgett technique in which the "self-assembly" of the monolayer at the air-water interface precedes film transfer onto a solid support. Hence, self-assembled monolayers or SAMs refer to monolayers formed directly *via* spontaneous adsorption (usually chemisorption) of molecules from solution or the gas phase onto a solid substrate. The order in the monolayer may not be perfect or crystalline. For example, monolayers of short-chain alkanethiols with less than ten methylene units on gold or silver, although less ordered compared with the long-chain alkanethiols, are also referred to as SAMs [13-14].

Brief Survey of SAMs. SAMs provide a means of fabricating interfaces with designed properties by direct spontaneous adsorption of the adsorbate species from solution to a solid surface. This procedure is applicable to systems wherein the adsorbate have functionalities that have strong binding specificity for the solid surface, for example, by chemisorptive interaction, and a relatively long alkyl tail that can condense into crystalline-like order that is similar to that of bulk,

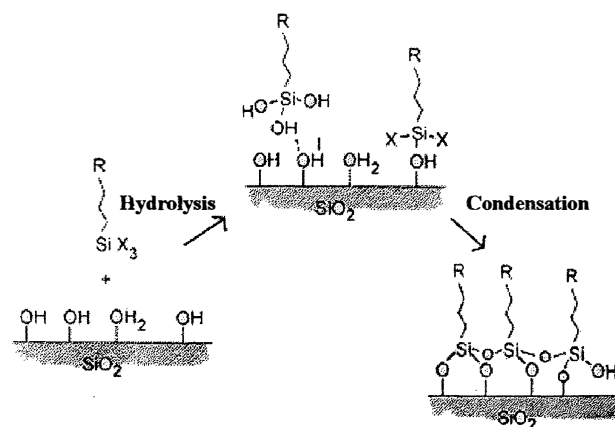


Fig. 2. Formation of alkylsilanes on silica surface; X represents either Cl or alkoxy group

paraffinic crystals (Figs. 1 and 2). Different systems have been investigated, organosulfur compounds on metals: gold, copper, silver [15] or semiconductor, GaAs [16]; silanes on glass [17], silicon [18] or mica [19]; and, carboxylates on metal oxide surfaces [20-21]. These systems generally form stable, ordered, and oriented monolayers at the substrate surface as shown in Figures 1 and 2.

SAMs on Gold. The sulfur-gold system for SAMs applications has the following advantageous features: gold is relatively inert to oxidation in air, in contrast to silver, copper and other metals; at the same time, a wide variety of molecules can be functionalized with the disulfide or sulfide moiety. Hence, SAMs on gold were used in numerous fundamental studies: wetting phenomena [22-23], adhesion [24], tribology [25], electrochemistry [26-27], protein adsorption [28-29], and cell-adhesion studies [30-31], among others. This adsorption system also found uses in the preparation of novel materials such as semiconductor nanocrystals [32] and in the preparation of ultrathin polymer films [33-35]. Furthermore, coupled with lithographic techniques, ordered arrays of different SAMs functionalities can be patterned onto surfaces resulting in structures with patterned wettability and adhesive properties [23].

Nuzzo and Allara [36] first reported the preferential and high affinity of the sulfur atoms to gold when examining the adsorption from solution of bifunctional organic disulfides (Fig. 3) to gold. Since then, the adsorption of disulfides and thiols to gold surfaces have been studied extensively. Nuzzo *et al.* [37] extended the system to other functionalized alkyl disulfides; the conclusion was that adsorption takes place through the sulfur atom preferentially over other groups such as hydroxyl, amino, carbonyl, chloride, methyl, phenyl, or nitro. Also, the monolayer films formed have dense coverages. The specificity of interaction

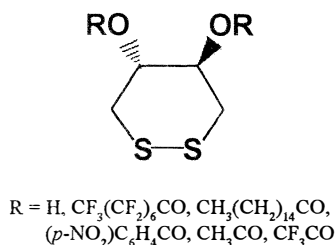


Fig. 3. Example of functionalized disulfide compounds that form SAMs on gold [36]

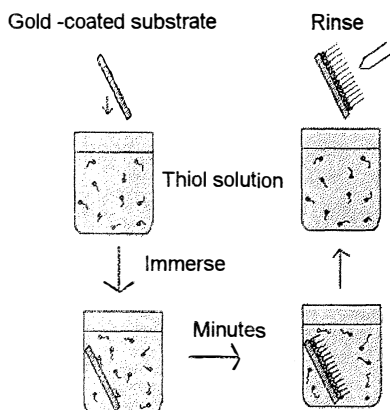


Fig. 4. Steps in preparation of SAMs on a solid substrate; in the example, an alkanethiol is adsorbed from dilute solution onto a gold-coated substrate

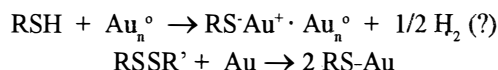
through the disulfide end of the molecule results in the orientation of the alkyl group or R chains (Fig. 1) toward the monolayer-air interface. In studies at ultrahigh-vacuum conditions, X-ray photoelectron spectroscopy (XPS) revealed that adsorption of dimethyl disulfide to gold involves scission of the disulfide bond and formation of a strong thiolate-gold bond [37]. The same type of linkage was confirmed for disulfides adsorbed from solution [38]. The thiolate S ($2p_{3/2}$) signal in the XPS spectrum appears at 162.0 eV while the bulk disulfide S($2p_{3/2}$) signal is at 163 eV [38].

Whitesides and co-workers [13] have also demonstrated that functionalized and non-functionalized alkanethiols of the form HS(CH₂)_nX [where X = CH₃, CF₃, CH=CH₂, OSi(CH₃)₂C(CH₃)₃, Br, Cl, OCH₃, SCOCH₃, CO₂CH₃, CN, OH, CO₂H] preferentially chemisorb to gold through the sulfhydryl tail group. The < 5 Å depth sensitivity of wettability measurements [40] confirms that the tail group X is indeed at the monolayer surface. Angle-dependent XPS additionally pinpointed the relative location of the heteroatoms as a function of depth from the monolayer-vacuum interface, and corroborated the idea that attachment was through the sulfur endgroup and that the X group was at the monolayer-vacuum interface. It is for this same reason that SAMs attracted the interests of many scientists because

it offers a method of functionalizing surfaces, which also provided model surfaces for understanding other phenomena. For example, a CF₃-terminated surface would have surface properties akin to Teflon. Already, many functional groups have been attached to alkanethiols, such as, electroactive organometallic moieties and biomolecules such as small proteins and peptides [41].

The monolayer at gold, when the number of methylenes in the alkyl chain exceeds 10, is well-ordered, densely packed, and oriented nearly perpendicular to the surface (Fig. 1) partly due to van der Waals interaction between chains [22]. The present consensus is that the alkyl chains for long-chain alkanethiols adsorbed on gold are tilted approximately 20° to 30° from the surface normal as inferred from a number of studies, e.g., ellipsometry [38] and infrared reflectance [42]; the molecular packing on Au (111) surface is believed to be $\sqrt{3} \times \sqrt{3}R30^\circ$ —that is, the sulfur atoms sit in three-fold hollow spaces between gold atoms and the sulfur overlayer packing is rotated by 30° from Au (111) lattice—based on electron diffraction studies of SAMs on gold single-crystal foils (Fig. 2) [26,43].

To date, it is not clear whether the reaction of the sulfide with gold liberates a proton or hydrogen molecule, although it is already proven that the interfacial reaction yields a relatively robust bond between gold and the sulfide or disulfide [41]:



The preparation of SAMs, particularly that on gold is straightforward. One needs to only immerse a gold-coated substrate in a dilute solution (~ 1-10 mM) of the organosulfur compound, and a robust, well-ordered SAMs forms in minutes (Fig. 4). However, the overall kinetics was found to involve a two-step process - first is the Langmuir-type adsorption behavior that occurs within a short time, and the slow (days) ordering or “crystallization” of the alkyl tail resulting in denser and closed-packed alkanethiols [41]. The polarity of the solvent also affects the order in SAMs; generally, a polar solvent, such as ethanol, favors formation of a polar activation state during equilibration of the thiol monolayer resulting in highly ordered SAMs [41].

SAMs on Silica Surfaces. Glass is amorphous silica (SiO₂) which has surface hydroxyls - silanol groups - (Fig. 3) and adsorbed water that can readily react with chlorosilanes and alkoxy silanes. This reaction has long been utilized in the functionalization of powdered silica for chromatographic applications, for example, in reverse-phase chromatography, the silica powder can be made hydrophobic by attachment of a monolayer of long-chain alkylsilanes to the surfaces of the particles. The reaction of chlorosilanes at the surface is a poly-condensation reaction yielding a strong covalent bond

at the surface. For alkoxysilane, usually methoxy or ethoxy silanes, the process occurs in two steps: hydrolysis and subsequent condensation reactions as schematically shown in Figure 2.

The silylation reaction is not only suitable for formation of single monolayer assemblies. It was recently reported that stacked layers of silanes can be formed from hydroxyl-terminated precursor monolayers [44]. This structure was the case for the multilayer assemblies with optical nonlinearity (NLO) by incorporation of NLO-chromophores within the multilayered assembly [44] (Fig. 5). The films were shown to possess stabilized, non-centrosymmetric ordering of the trapped NLO-chromophores; such a material would have potential application as optical waveguide or in frequency-doubling of laser light. Frequency-doubling of red to blue laser, for example, would allow reading and storage of higher density data in optical storage devices than those presently used. More recently, a self-replicating supramolecular assembly of amphiphilic silanes was reported by Sagiv and co-workers [45], where sequential treatment of acetone with residual water and octadecyltrichlorosilane (OTS) results in intercalation of OTS bilayers in between an initial bilayer of oxidized nonadecyltrichlorosilane-OTS layer (Fig. 6). The intercalation technique is yet to find direct application in incorporating novel molecules, but the fabrication methodology opens up a new route to forming supramolecular assemblies, akin to the Langmuir-Blodgett methodology discussed below.

LANGMUIR-BLODGETT FILMS

The Monolayer at the Air-Water Interface. As defined previously, the fabrication of monolayer films on solid substrates may be preceded by organization of the molecules at the air-water interface prior to transfer. Similar to SAM's,

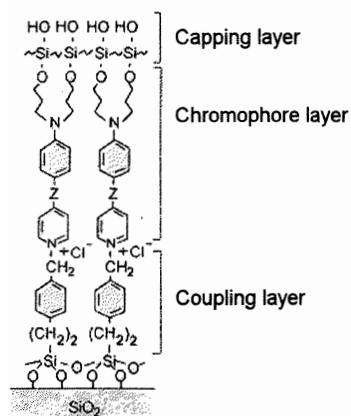


Fig. 5. A non-linear-optically (NLO-) active multilayered structure prepared by a sequential self-assembly process [44]. The procedure allows unidirectional orientation of the NLO chromophore which yields a net, noncentrosymmetric order in the film.

the molecules must be amphiphilic in nature—thus, the polar end group is submerged in the water phase (subphase) and the hydrophobic tail end is directed towards air. This orientation of amphiphilic molecules results in a net lowering of surface free energy (or surface tension, γ). These monolayers at the air-water interface and their transfer to solid substrates were extensively studied by Irving Langmuir [46] in the 1920s using the now so-called Langmuir trough (Fig. 7). The build-up of multilayers were introduced by Katharine Blodgett [47]; thus, the now popularly known Langmuir-Blodgett (LB) films. Since then, their technique gained popularity (see for example, Sobotka [48]) that continues to this day. A classic text in the field was published by Gaines [49]. Similarly, the wide interest in the technique is motivated by its potential to “molecular engineer” the physico-chemical properties of the LB-films, which in turn promises potential applications such as in the development of opto-electronic devices [4,50]. Additionally, the technique was widely adopted to prepare model biological membranes [51]. Originally, the procedure was limited to amphiphiles, such as fatty acids and phospholipids. However, the methodology has also been applied to polymeric systems [52-54].

The monolayers at the air-water interface can be formed in two ways: one, it can form as a result of adsorption of the amphiphilic molecules from solution (the subphase) at the air-water interface. In this type, the interfacial monolayer is in equilibrium with the dissolved phase; this is generally termed as a “Gibbs monolayer” in view of an adsorption behavior defined by the Gibbs isotherm. Another way is to spread a dilute ($\sim 1\text{mM}$) solution of the amphiphile in an organic solvent (usually methylene chloride or hexane) onto the water surface, and then allowing the solvent to evaporate. The insoluble molecules remain on the surface; this type is referred to as “spread monolayers” or “insoluble monolayers.”

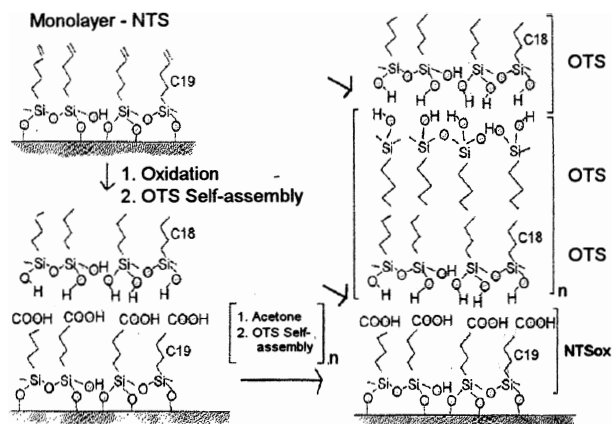


Fig. 6. Multilayered SAMs by intercalation of octadecyltrichlorosilanes (OTS) within the polar regions of the film (insertion regions are indicated arrows). Treatment with OTS for n times yields multilayers with $2^n - 1$ OTS layers [45].

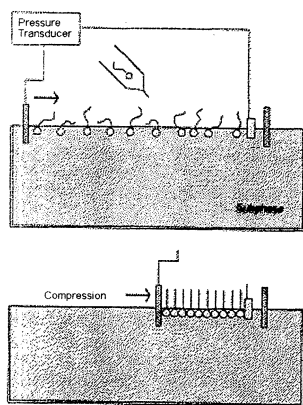


Fig. 7. The Langmuir-trough. Initially, a dilute solution of the amphiphiles is spread at the water surface. Surface pressure changes on compression with the moving barrier is followed by a pressure transducer or film balance.

The latter type is more popular in monolayer fabrication because the density of packing of the monolayer can be directly controlled by compression. This is done on a Langmuir trough which consists of non-adsorbing barriers (polytetrafluoroethylene, Teflon, is used nowadays, but in the days of Langmuir, waxed thread was used). One barrier is movable, and the other fixed, which can also act as a film balance to measure the surface pressure, π . The surface pressure is the lowering in the surface tension of the subphase (γ_0) on spreading and compression of the insoluble monolayer (γ):

$$\pi = \gamma_0 - \gamma$$

The surface pressure may be measured either by a torsion wire or a Wilhelmy plate and balance [55]. The film balance may be connected to the moving barrier in a feedback loop which allows control of surface pressure when transferring the monolayers onto solid substrates.

The surface pressure is dependent on the surface area available to the amphiphiles. The curve obtained on compression as a function of area in terms of area per molecule is the surface pressure-area (π -A) isotherm as shown in Figure 8, which is typical for a fatty acid. The isotherm is a two-dimensional analog of the pressure-volume isotherm: at large areas, the behavior and separation of molecules are gas-like (highly compressible region); at intermediate areas, the surface pressure increases more steeply on compression (low compressibility). Phase transitions in the monolayer are signified either as a change in slope or as a plateau which indicates a two-phase region. For fatty acids, the liquid phase is a liquid-expanded phase initially, and further compression forms a so-called liquid-condensed phase, followed by a solid-like film until the monolayer buckles and finally collapses.

The character of the π -A isotherm depends on a number of factors: intermolecular interactions, the size of the head group, length of alkyl tail, subphase pH and composition, and temperature. For example, long-chain fatty acids such as octadecanoic acid ($C_{17}H_{35}CO_2H$) and hexatriacontanoic acid ($C_{35}H_{71}CO_2H$), register the same limiting area (the extrapolated area of the steep curve at zero pressure) of 2.0 nm^2 , which is the cross-sectional area of alkyl chains oriented in a close-packed monolayer normal to the interface [56]. However, the collapse pressure is different for the two fatty acids, owing to the difference in the length of alkyl tail, and therefore different extent of intermolecular forces within the monolayer [56]. For mixed monolayers, the π -A isotherm would also depend on composition.

The phase behavior and flow properties of the monolayers at the air-water interface can be followed by a number of techniques: a layer of talcum powder floated at the surface would show the compression behavior, fluorescent dyes as probe may be incorporated and imaged using a microscope, or the monolayer may be directly imaged by Brewster angle microscopy [56]. The structure of the monolayer at the interface has also been monitored by a number of techniques as summarized in Table 1.

Film Transfer. Transfer of the monolayer at the air-water interface onto solid supports can be achieved in two ways: either by vertically dipping or lifting the solid substrate through the interface or by horizontally touching the solid surface, the so-called Schaefer method [49]. In the vertical film transfer, one may keep the surface pressure constant, keeping a constant structure of the monolayer during deposition. Nevertheless, the monolayer may experience distortions due to shearing by capillary forces as the interface wets the substrate. To circumvent this distortion, the mild deposition technique by the Schaefer method is usually used.

There are three general types of multilayer vertical depositions: X-type for transfer on the downstroke only, Y-type for transfer on both up- and downstroke forming head-

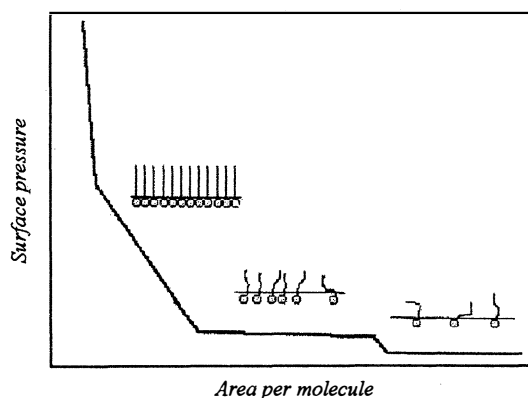


Fig. 8. A hypothetical π -A isotherm for a fatty acid monolayer at the air-water interface

Table 1. Techniques for Characterization of Insoluble Monolayers at the Air-Water Interface and Monolayers Transferred onto Solid Substrates [56].

Technique	Parameters Measured	Information Obtained
Surface pressure*	π (mN/m) versus A/molecule	Limiting area, collapse pressure, state of monolayer
Surface potential*	ΔV (mV) versus A/molecule	Surface dipole, headgroup orientation
Surface viscosity*	η_s	Viscosity changes
Ellipsometry	Polarization of reflected light	Refractive index and thickness of the monolayer
X-ray diffraction (from synchrotron source)	Reflectivity	Lattice spacing and structure in high-density monolayers
Neutron diffraction	Reflectivity	As for X-ray diffraction, but contribution from water reflectivity is eliminated
Second-harmonic generation	χ^2	Average molecular orientation
Reflection-absorption FTIR spectroscopy (RAS-FTIR)	Reflectance spectrum	Average molecular orientation
Fluorescence microscopy	Fluorescence of probe molecule	Phase behavior and monolayer structure

*Characterization of monolayers at the air-water interface only

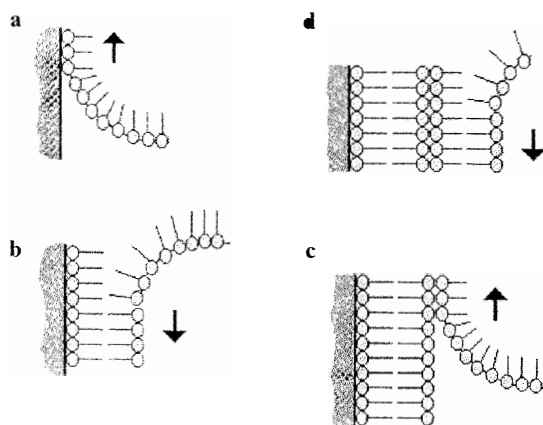


Fig. 9. Schematic of multilayer deposition of amphiphiles by the LB technique: (a) initial monolayer deposition onto a hydrophilic substrate on the first upstroke; (b) transfer on the downstroke for a hydrophobic surface; and, (c-d) sequential upstroke and downstroke in Y-type film transfer

head and tail-tail bilayers, and Z-type for upstroke transfer only (Fig. 9). By far, the most common for amphiphiles is the Y-type film transfer. It is exhibited by fatty acids on hydrophobic surfaces or a hydrophilic substrate which has already formed a hydrophobic coating layer after a first upstroke. The film transfer ratio is usually measured as the area lost at the air-water interface divided by the area of the substrate (multiplied by two since transfer may occur on both sides of the substrate) and gives an indication of monolayer quality. Transfer is usually optimized by the dipping and withdrawal rate of the substrate through the interface, temperature, and subphase composition. For example, in the case of long-chain fatty acids, stable and high-quality films with low defects are usually formed when the subphase used is a dilute CdCl_2 solution (~ 0.1 mM) at 20°C and pH of 5-6 [56]. Apparently, the interaction of the Cd^{2+} with the acid

headgroups allows an optimized packing structure of the monolayer, as observed in the nearly vertical orientation of the alkyl tails in the presence of Cd^{2+} compared with tilted chain orientation in the absence of Cd^{2+} .

COMPARISON OF SAMs AND LB FILMS

Perhaps a major drawback of the Langmuir-Blodgett deposition is the film integrity and stability. LB films are not as strongly bonded to the substrate compared with the SAMs; in the former, the film is only physisorbed at the substrate surface whereas in SAMs, stronger chemisorption takes place. Although many alternatives to deposition of LB films have been proposed for faster, automated deposition, it is still relatively more tedious compared with direct adsorption by self-assembly. The LB film allows multilayer formation, but it has also been demonstrated to be possible in the self-assembly of functionalized thiols on gold and silanes on hydroxylated surfaces [41].

A NOTE ON THE SUBSTRATE

To date, SAMs of organosulfur compounds are best prepared on gold, as pointed out earlier. High purity gold (99.99%) is typically resistively or e-beam evaporated at high vacuum conditions ($\sim 10^{-6}$ torr) while exposing various substrates (usually, glass or silicon) to the vapor. This procedure produces polycrystalline gold surface with grain size ranging from 10^2 to 10^3 nm diameter. This surface is rough surface at the molecular level. Thus, the alkanethiol could follow the topography of the surface or form bridges such as shown in Figure 10. Bridging was also suggested to occur for LB layers of amphiphiles, particularly under conditions of transfer ratios of one (where the area lost at the air-water interface equals the geometric area of the substrate) [49]. In the case of alkylsilane, bridging is intuitively most plausible since the siloxane moieties could form a stable two-dimensional network at the interface.

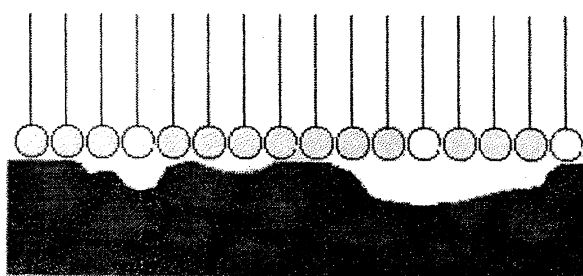


Fig. 10. Schematic of possible bridging of monolayer films on a rough surface.

The cleanliness of the substrate is also a crucial factor for preparation of molecular films, since obviously, impurities would affect the quality of the films produced. However, ambient to clean room conditions were usually sufficient, particularly for the thiol-gold SAMs where the thiol with its strong preference for gold would simply displace weakly adsorbed impurities at the gold surface. In the case of alkylsilanes, the amount of water adsorbed on the substrate is critical in forming good monolayers, since there is tendency for the silane to polymerize on hydrolysis. The LB technique is best done in clean room conditions because dust particles at the air-water interface will disrupt formation of compressed monolayers.

SOME APPLICATIONS

Early after development of the LB technique, Blodgett demonstrated that the thickness of the film can be adjusted by the number of layers deposited (for example, C_{16} , C_{18} , and C_{20} fatty acid calcium salts have thicknesses per layer of 2.15, 2.44, and 2.74 nm, respectively) which she utilized in preparing nonreflective glass, and a film-thickness gauge based on the interference of visible light reflected from LB films of varying film thicknesses resulting in various colors [56]. Langmuir and co-workers also developed a sensor-type device based on the change of thickness of the overall layer upon adsorption of other substances on the film; again based on color changes of the layers when adsorption occurred.

The two methodologies: self-assembly and LB-deposition find many potential applications. They may also be used in tandem. As an example, Aizawa and co-workers reported an optical immunosensor based on protein monolayers deposited by LB technique [57]. Their procedure, however, also called for first making a SAM of alkylsilane to make a quartz surface hydrophobic. The hydrophobic quartz was then used for subsequent LB-deposition of a bilayer of Protein A (Fig. 11). This protein has specific affinity for anti-human IgG antibody. The antibody was "self-assembled" from solution onto the Protein-A monolayer on quartz, and the final, composite layer was used in optical immunosensing studies using a fluorescent dye. The immunosensor was found to detect human IgG concentrations of 10^{-4} to 10^{-7} g mL $^{-1}$.

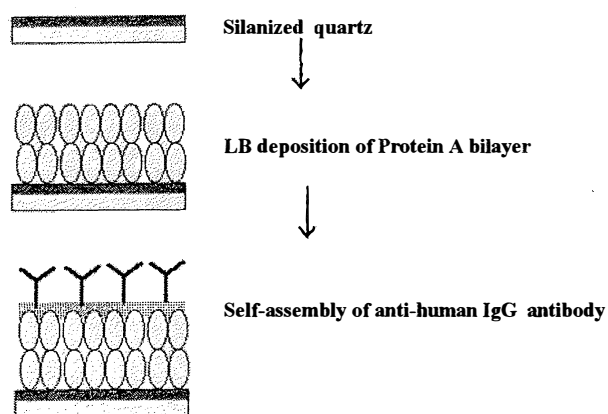


Fig. 11. Steps in the fabrication of an optical immunosensor for human IgG [57]

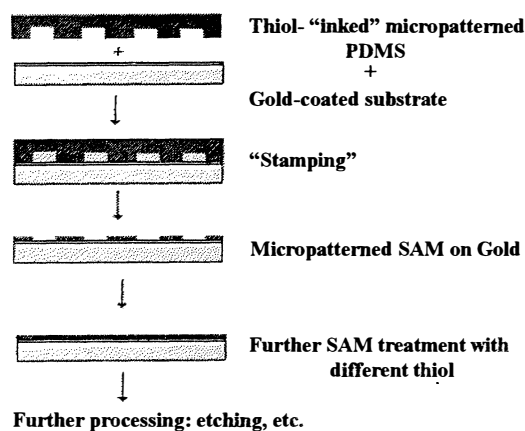


Fig. 12. Steps in microcontact printing using SAMs on gold; PDMS is polydimethyl siloxane [58]

Recently, SAMs on gold found utility in microcontact printing [58]. This procedure involves "inking" an elastomeric "stamp" (polydimethylsiloxane) with the alkanethiol. The inked lithographically-patterned stamp was then pressed onto gold substrates. Alkanethiol SAMs formed on contact areas with gold, thus protecting it from a subsequent chemical etching of unprotected gold (Fig. 12). This procedure also allows derivatization of unprotected gold areas with other functionalized thiols. Microcontact printing was found to be a facile procedure for making micron- to nanometer-size patterns even on curved surfaces, which could find applications in opto-electronic device fabrication and as resists for further processing [58].

CONCLUSION

The scientific literature abounds with many reports on preparation of molecular assemblies on solid surfaces, either by Langmuir-Blodgett or self-assembly technique. These procedures allow nanometer control of structure and organization of the molecular assembly. The many potential

applications of these materials could pave the way for the next generation of molecular nanodevices.

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