Organized Molecular Assemblies

George M. Whitesides, Cochairman

Harvard University

Gregory S. Ferguson, Cochairman

Lehigh University

David Allara

Pennsylvania State University

Dan Scherson

Case Western Reserve University

Lois Speaker and Ari Ulman

Eastman Kodak Company

ABSTRACT: Self-assembled monolayers (SAMs) are part of a class of organized molecular assemblies (OMAs) that represent a major new theme in condensed-matter science. The characteristics of SAMs and a summary of research recommendations are first presented in an executive summary. After introducing the definitions and characteristics of OMAs in which Langmuir-Blodgett (LB) films are compared with SAMs, the opportunities for scientific study, technological applications of SAMs, and limitations to transferring scientific understanding into technology are discussed. The discussion of SAMs includes the scientific opportunities in condensed-matter science, heteroepitaxy, and nanostructures; the technological applications in fuel cells, photoelectrochemistry, polymer/metal (oxide) interfaces, and thin-film, multilayer, solar collectors; and the limitations of stability, monolayer-substrate interactions, and mechanical stability for the transfer of science into technology. After providing an overview and discussing potential payoffs from research, the needs and opportunities are summarized for tribology, fuel cells, photovoltaic cells, electrochromic windows, surface contamination, selectivity, and fouling in membrane separations, biosurfaces, sensors, and corrosion.

I. INTRODUCTION

Organized molecular assemblies (OMAs) — self-assembled monolayers (SAMs), Langmuir-Blodgett (LB) films, vesicles, and lipid bilayers — represent

---

a major, important new theme in condensed-matter science. SAMs, in particular, have properties suggesting potential wide applicability in control of interfacial properties for systems of interest to Department of Energy (DOE). SAMs are systems at or close to thermodynamical minima, and are thus easy to prepare. The production of SAMs, unlike most surface technologies, is straightforward, and they are intrinsically manufacturable: they form highly ordered films by simple, low-cost processes, and they have low defect concentrations.

A. Characteristics of SAMs

We note these characteristics of SAMs as particularly relevant to the DOE mission:

- SAMs can be formed on rough, irregular, and shaped surfaces as well as on inner surfaces and surfaces not accessible to line-of-sight methods.
- Damaged SAMs can be regenerated *in situ*, if the appropriate molecules are present in the immediate environment (i.e., as components in corrosion-, friction-, or soiling-control systems).
- The properties of SAMs can be varied with great flexibility by control of their molecular components.
- Because the components of SAMs reliably form monolayers, small amounts of material will cover large surface areas: typically 1–10 kg of material might provide monolayer coverage of 1 km^2 of substrate. Processing with SAMs is thus intrinsically economical and applicable to large-scale materials problems.

B. Recommendations for Research

1. Research in OMAs should focus on SAMs. LB films have certain applications in multilayer systems and in research (e.g., in optics), but the simplicity and economy of formation of SAMs and their applicability to rough, shaped, and interior surfaces make them much more promising for large-scale, cost-sensitive applications.

2. Support should be directed toward single-investigator projects. The style of research in SAMs focuses on small, individual research groups working alone and cooperatively. Instrumentation at the $100-K to $1-M level, which is often not shared, is an important component of this research. Large national facilities (light sources, etc.) are not crucial to the most important work in the field, although certain problems require access to these facilities. The national laboratories have not, so far, played a significant role in

the field, but might constitute a valuable resource at the technology-development stage.

3. The most important areas for basic research are

  a. Development of methods for forming in-plane patterns and features in SAMs

  b. Use of SAMs for two-dimensional (2-D) organization of complex molecules

  c. Studies of SAMs as model systems for complex phenomena, including, but not limited to, wetting, adhesion, friction, wear, interactions at biosurfaces, fouling, soiling, and corrosion

  d. Use of SAMs to study phenomena in condensed-matter science: cooperative behaviors, phase separations, and the influence of defects

  e. Use of SAMs to nucleate growth of condensed phases in three dimensions: condensation of water, growth of crystals, attachment of polymers

  f. Development of new types of SAMs, especially those with enhanced stability, and new types of surface-monolayer chemistry

  g. Development of computational models for SAMs and SAM-related phenomena.

4. The most important areas for generic applied research are

  a. Development of thermally and oxidatively stable SAMs formed from stable organic and inorganic components

  b. Direct application of SAMs to the most important classes of substrates — steels, aluminum, copper, semiconductors, ceramics, glass, and photolytically stable polymers.

5. Areas for applications research involving SAMs are

  a. Corrosion inhibition — development of self-regenerating, passivating systems based on SAMs

  b. Tribology-control systems — development of new, robust, self-regenerating systems for control of friction

  c. Soiling-control systems — use of SAMs to develop easily cleaned surfaces (low-surface free-energy fluorocarbons, surface-attached hydrogels) for

optical components and surfaces resistant to soiling and biofouling for membranes and subsurface and marine structures

d. Fuel cells — controlling interfacial properties in gas/liquid/catalyst/membrane systems to improve performance.

SAMs are valuable in research as model systems for establishing the fundamental mechanisms of complex phenomena like corrosion, friction, wetting, wear, adhesion, biofouling, and surface-charge dissipation. These studies will guide the design of coatings and thick films for practical applications for which SAMs are not sufficiently strong, stable, or robust. The most serious deficiency of SAMs in practical applications is their thermal, mechanical, and oxidative instability. Known systems are limited to temperatures below approximately 150°C, unless they can be used in self-regenerating form. The strategy of self-regeneration at a surface, accomplished *in situ* by including the molecular components of the SAM in the surrounding fluid or vapor, constitutes a unique and valuable characteristic of self-organizing systems.

LB films and other types of organized assemblies will also be useful, especially in research applications and in high-value uses such as optical and electro-optical devices.

II. DEFINITIONS AND CHARACTERISTICS

Although the LB technique provided the first practical laboratory technique for constructing ordered molecular assemblies in the laboratory, this report focuses on self-assembled (SA) systems.[1,2] This focus by no means diminishes the importance of LB technology,[3] but applications in the transportation and utilities technologies require emphasis on issues such as ease of film fabrication, stability, and cost — those that favor SAMs over LB films. This report deals with monolayers, although methods for fabrication of self-assembled multilayers based on molecular self-assembly have been developed in the past decade.[4]

SAMs are OMAs that form spontaneously by adsorption of amphifunctional molecules at solid-liquid and solid-gas interfaces. These adsorbates have strong affinities — usually chemical in nature — to the substrate surfaces. The spontaneity of monolayer formation implies that such systems are thermodynamically stable. They are more stable than LB films, whose molecular components are often physisorbed to the surface of the substrate. That SAMs form *in situ* indicates that partially formed, disordered monolayers can be driven to complete, ordered systems, and that monolayers can self-regenerate in the presence of a molecular adsorbate.

There are many types of SAMs, including carboxylic acids on Al_2O_3, Ag_2O, and glass; phosphonic acids on di- and trivalent metal oxides; sulfonic

acids on Ag_2O; disulfides and thioethers on gold; thiols on gold, silver, copper, and platinum; alkylsiloxanes on hydroxylated surfaces (Al_2O_3, SiO_2, glass, etc.); alcohols and amines on Pt. Common to the formation of all SAMs is an exothermic chemisorption step (e.g., ca. 40 kcal/mol for long-chain alkanethiols on gold) that provides most of the driving force for the process. The exothermicity of this chemisorption indicates that, unless there are interfering factors, these systems will maximize the number of adsorbed molecules on the surface, and generate a close-packed and ordered assembly. The other major contributions to order and stability in SAMs are interactions between the adsorbed chains (van der Waals, hydrogen bonding, etc.). The stabilization afforded by these interactions can be comparable in magnitude to the energies of chemisorption; for example, the van der Waals interactions for $C_{16}H_{33}S/Au(111)$ amount to approximately 26 kcal/mol.

The spontaneity of formation and high packing densities in these systems leads to films with few defects. This characteristic is important when considering issues such as wetting, tribology, and electron transfer. The amphifunctional character of the molecules that form SAMs and the flexibility in molecular structure offered by organic synthesis provide the capability to tailor surfaces and to control their physical and chemical properties.[5] Incorporating functional groups into the alkyl chains of the adsorbates will allow the synthesis of increasingly more complex systems. Such studies are vital both to detailed understanding of self-organization and to the development of advanced materials and their applications in technology.

To summarize, the properties of SAMs most important in technology relevant to transportation, utilities, and conservation are

- Spontaneity of *in situ* formation
- Thermodynamic stability
- Ability to apply conformal coatings on surfaces, regardless of their shape
- High packing densities and low defect concentrations
- Molecular alignment
- Capability to tailor surfaces to desired applications
- Synthetic flexibility.

III. SCIENTIFIC OPPORTUNITIES

Unique opportunities for increasing our understanding of thin-film structures, surfaces, and interfaces involving molecular materials are available to researchers who use SAMs. These fundamental studies will have broad importance in the areas of materials science, condensed-matter physics, chemistry, and the biological sciences. They will have broad relevance to generic problems in surface and interface modification and to certain classes of problems in manufacturing and energy conservation and generation.

A. Condensed-Matter Science

Recent applications of SAMs to the physics of 2-D condensed matter are particularly interesting. SAMs provide the opportunity to study the effects of dimensionality in phase transitions and the correlations between phase states, structural coherence, and molecular size and shape. The highly controlled surface structure in SAMs also provides opportunities for new experimental approaches to understanding the difficult problem of nucleation and growth of molecular crystals. In this context, biomimetic nucleation of crystal growth represents a growing area of research relating to SAMs that offers exciting opportunities for fundamental study in materials science.[6] The organization of crystalline materials on modified surfaces should not be limited to inorganic salts but should be viewed as a more fundamental phenomenon. Nonetheless, establishing the rules governing biomineralization may provide inexpensive routes for the production of ceramic materials that are of interest to DOE.

B. Heteroepitaxy

One of the premier issues in materials science today is the question of how to accomplish heteroepitaxy: that is, how to fabricate the most defect-free interface between a crystalline substrate and a deposited, crystalline overlayer of another material with different lattice constants. A well-known, purely inorganic example is the continuing effort to grow GaAs on silicon by molecular-beam epitaxy. Creative uses of SAMs, with appropriate chemical and thermal stability, as templates to assist such heteroepitaxy by fine-tuning changes in lattice spacing over molecular distances, would be of great interest.

C. Nanostructures

Another area of great importance at the intersection of materials science and physics is the fabrication and electronic properties of surface structures patterned at the nanometer scale.[7] High-resolution, lithographic processing demands the use of resist films with nanometer-scale thicknesses and low defect concentrations. The combination of high chemical flexibility and other suitable properties makes SAMs an attractive possibility.[8] The ability to create structures such as nanowires and quantum dots has been a key factor in the development of the physics of quantum confined structures. Another intriguing possibility in materials science is that of using SAMs for information storage applications. One approach is suggested by the work of Fujishima and co-workers.[9] This group used the optically induced isomerization to modify the redox potential of surface-confined species in an LB film. The resulting heterogeneities in the film could be read by simple electrochemical methods.

There are several major opportunities to use SAMs to help resolve long-standing scientific issues in the chemical sciences. The high flexibility to synthesize surfaces with well-defined arrays of functional groups should continue to provide major advances in the understanding of wetting and surface chemical phenomena. This research will provide new understanding of the complex interfacial behavior that underlies the performance of a range of natural and synthetic structures, including environmentally protective coatings, biocompatible surfaces, highly specific biological receptor sites, and advanced composite materials. Studies of the organization of complex molecules, polymers, oligopeptides, and other biomolecules are important to derive an understanding of the relation between the structure of an individual molecule and its organization in two dimensions. Such fundamental understanding is vital for the advancement of materials science.

IV. OPPORTUNITIES FOR APPLICATIONS IN TECHNOLOGY

Beyond the fundamental studies, there are now a number of problems in technology to which SAMs and other OMAs can be applied.[10] The following list is incomplete, but it provides examples that illustrate the types of problems for which SAMs may provide solutions.

A. Fuel Cells

A broad range of problems in the technology of phosphoric acid-organic membrane fuel cells centers on the control of interfaces, and SAMs may be useful in solving a number of these problems. Among the potential applications are

- Controlling the wettability of pores in the gas-distribution membranes to facilitate the transport of gases to the cathode and anode surfaces, to control the wetting of these and surrounding surfaces, and to control the removal of water from the cathode
- Controlling the interface between the platinum and the carbon support to limit corrosion
- Controlling the interface between the carbon and the ionomer surface layer to ensure good proton conductivity
- Improving adhesion between the catalyst-containing surface ionomer layers and the central ionomer membrane

SAM-forming additives may, speculatively, be useful in controlling the kinetics of redox processes at the interfaces. An oxygen reduction catalyst that would adsorb at the cathode surface and increase the rate of reduction of O_2 to water would lead to large improvements in cell performance. By using a self-regenerating layer, it would be possible to compensate for material lost by corrosion or electrochemical damage.

B. Photoelectrochemistry

Monolayer films offer interesting opportunities in electrode modification. The simplest, yet most important, application is electrode passivation, especially for materials like amorphous silicon, which are unstable in aqueous media. Using simple n-alkyl derivatives as adsorbates for passivation introduces an insulating layer at the electrode, thus decreasing electron transfer and cell performance. Using more conductive derivatives, however, would overcome this problem. New possibilities have been reported recently for the stabilization of semiconductor interfaces.[11] SAMs have been demonstrated to provide useful protection of metal (Cu, Au) surfaces against chemical corrosion. Adsorption of a SAM on a photoelectrode may also help to passivate surface states, and thus reduce losses in efficiency due to electron-hole recombination without inhibiting electron tunneling across the interface.

Synthetic models for photosynthesis may be important for engineering specific photoelectrodes. Modifying these electrodes with appropriate monolayers would result in a modified potential that can carry out a specific, clean chemical reaction. Advances in photo electrochemical catalysis may also result from research on SAMs, although it would likely require the use of organometallic derivatives.

C. Thin Film, Multilayer, Solar Collectors

OMAs should be useful in addressing those problems with photovoltaic (PV) panels and concentrators, solar collectors, and electrochromic (EC) windows that require tuning of surface properties. Current spending for research on PV modules is about $40 M/year, with only $600 K set aside for encapsulation studies. PV efficiencies have reached more than 17%, and operation at this efficiency for 30 years would make these modules economically viable.

The lifetime of PV modules is currently limited by the photothermal degradation of the polyethylene vinyl acetate (EVA) copolymer presently used as a protective coating. This photodegradation causes the film to darken and leads to losses of 5 to 15% (or more, in some cases) during 5 to 10 years of operation in hot, dry climates. This process proceeds most rapidly from the interface between EVA and the soda lime glass superstrate as well as from around the "fingers" of metallization that protrude into the film. Replacement of EVA is now being considered, but similar photodegradation problems will likely be encountered with other polymeric layers, especially at the metal (oxide)/polymer interfaces. The photochemical stability of these sensitive interfaces may be significantly enhanced by SAMs used as low-dielectric coatings that also serve as diffusion barriers between different layers.

The efficiencies of flat-panel PV arrays, PV concentrators, and the heliostats of mirror fields are reduced by repetitive cycling (through soiling and cleaning) that accompanies environmental exposure. Exploratory work indicates that soil retention can be mitigated, and possibly eliminated, by treating the outer surfaces

with a single oriented layer of a fluorinated amphiphile. Samples treated in this way retain their original reflectances for more than a year and through 20 soiling/cleaning cycles. Longer term studies are required to determine specific lifetimes.

EC windows have a minimum of five layers of active materials and eight interfaces, including poorly understood interfaces between ion-storage and ion-conducting layers as well as interfaces from a superstrate and substrate. The barrier and dielectric properties of SAMs at these interfaces might play an important role in maintaining layer segregation and operating efficiencies. Antisoiling SAMs at the outer surfaces may also be beneficial.

D. Polymer/Metal (Oxide) Interfaces

SAMs offer potentially significant benefits in systems that require strong bonding between a metal (oxide) substrate and a polymer. These systems include conformal coatings of protective films, adhesives, primers, and paints. As mentioned in the opening section of this chapter, the formation of SAMs is driven by strong chemical bonding of the adsorbates to the substrate. Adsorbates may be modified by organic synthesis, before or after adsorption, to incorporate reactive end-groups that can be used to covalently attach a polymeric coating to the surface. The high packing densities, low-defect concentrations, and molecular alignment of these films should provide efficient multisite linkages between the substrate and the polymer.[12]

This technology may also offer advantages in reducing the number and/or complexity of required processing steps for fabricating metal (oxide)/polymer materials. As an example, a critical concern in forming a strong adhesive bond is the cleanliness of the substrate. In a typical preparation of a SAM, however, the desired adsorbate displaces physisorbed organic contamination, and the monolayer film is usually less prone to contamination than the bare metal (oxide). Hence, the process is, in some circumstances, self-cleaning and self-passivating. As the number of systems known to form SAMs grows, the need for some processing steps (e.g., removing the native oxide from the substrate) may also become unnecessary. Elimination of processing steps is advantageous both economically and in terms of environmental impact.

V. TECHNOLOGICAL PROBLEMS: LIMITATIONS TO THE TRANSFER OF SCIENCE INTO TECHNOLOGY

Basic research has established a range of properties for the most useful OMAs — SAMs formed by spontaneous chemisorption of organic molecules onto surfaces — that make them potential solutions to a broad range of technological problems of concern to DOE. The most relevant of these properties involve the ease and economy with which SAMs can be formed, and the flexibility with which their properties can be tailored by controlling the structures of the component

molecules through synthesis. Because these systems are at thermodynamic minima, they are intrinsically defect free and self-healing. SAMs form with high degrees of order on exposure of the surface to the adsorbing species; the technologist does not have to stabilize a metastable system. Clean-room conditions are not needed in SAMs preparation; their enthalpy of formation is often enough to clean the substrate surfaces by displacing dust and weakly adsorbed contaminants. SAMs will cover defects and can be formed on irregular and interior surfaces.

The major limitations to the application of SAMs in many technologies are their limited thermal, photochemical, and oxidative stability; an incomplete base of knowledge to guide their formation on many classes of substrates; and their low mechanical strength. Each of these limitations can be circumvented or minimized by developments of existing science or by extension of already demonstrated paradigms to new classes of materials.

A. Stability

Most work with SAMs has focused on components derived from polymethylene-based organic molecules $X-(CH_2)_n-Y$ in which the X group forms a bond with the surface and the Y group provides the function or tailors the interfacial properties. The polymethylene chain is subject to thermal damage; the chain oxidizes relatively readily in contact with air at temperatures greater than 100°C. For many applications, higher stability is required.

The obvious approach to this problem is to develop SAMs based on polymeric models of known stability. For example, components for SAMs may be based on polyarylsulfones and -ethers, polyimides, poly(diorganosiloxanes), fluorocarbons, polyphosphazines, and a range of other polymer structures that are already used for applications that require stability under extreme conditions. These systems could be modified for use in SAMs, either as functionalized oligomers or as functionalized polymers.[13] SAMs prepared from these structures can be confidently predicted to show much greater thermal and oxidative stability than those now known. It is probable that appropriate representatives of these systems will be usable in applications requiring exposure to air at temperatures of approximately 300° to 400°C for short times. For higher temperature applications, it will be necessary to make a greater step in technology. In principle, it should be possible to build SAMs of inorganic components with very high stability (carboranes, metal oxide clusters), but these types of systems have not yet been explored.

B. Monolayer-Substrate Interactions

Much of the research on SAMs to date has focused on well-defined, convenient model substrates: gold and silver, alumina, silica, and mica. Other metals and metal oxides have been surveyed casually, and there is every reason to expect that SAMs with high order can be formed on a range of substrates, but the appropriate surface chemistry for forming SAMs on "real" materials — native

oxides on steel, aluminum alloys, copper, bronze and amorphous silicon, multi-component silicate glasses, silicate minerals, concrete and others — have not yet been developed. A program to develop the surface-coordination chemistry appropriate for these substrates will be essential. The broad principles to be followed are well known, but the practical details remain to be established.

C. Mechanical Stability

SAMs typically have thicknesses of the order of 1 to 5 nm. They will not be mechanically strong. Even if they were, the underlying substrates would fail under the same mechanical stresses as they would if unprotected. The appropriate strategy for using SAMs to protect against mechanical wear will be to take advantage of their capability for *in situ* repair. Thus, for example, for a SAM to be useful in the control of friction or corrosion in an application in which mechanical damage or wear is probable, the wear surface should be exposed to a solution or vapor of the molecules making up the SAM. Wear will occur, but the SAM will regenerate itself *in situ*. For a solution to be used in cleaning exposed surfaces of PV systems, the components of a surface-protective SAM can be included in the cleaning solution. This capability for *in situ* regeneration is well established in model systems and is the basis for the use of fatty acids and derivatives as additives for control of corrosion, wetting, and friction. These types of self-healing processes must, however, be studied in greater detail to provide a science and engineering base appropriate for design in new applications.

D. Other Applications

There are many other potential applications of SAMs in the development of new technologies. For example, SAMs could be used as "masks" to control deposition of metal oxides or metals in new types of coating or electrodeposition processes. Existing systems are already excellent wetting and adhesion promoters, but have not been developed for processes involving painting or adhesion and wetting in manufacturing applications.

E. Recommendations

The highest-priority generic opportunities for moving SAMs into technology are

*   To develop SAMs with high thermal and oxidative stability
*   To develop the surface chemistry necessary to form SAMs on important classes of materials (steels, metal oxides, semiconductors, other metals, and ceramics)

- To develop and demonstrate strategies for regenerating SAMs *in situ*, especially under conditions in which wear or mechanical damage may be important.

VI. NEEDS IN RESEARCH

A. Overview

Multidisciplinary approaches to research and research instrumentation are two issues that must be properly addressed and resolved to ensure rapid and efficient progress in capitalizing on the scientific opportunities and solving the technological problems mentioned in the previous section.

At this stage of development in the field of SAMs, the problems are primarily those of the chemical sciences. In parallel with the typical structure of an inorganic substrate and a chemically bonded organic overlayer, a typical research group poised for the fastest advancements in the field might be one combining the skills of traditional disciplines of inorganic, organometallic, and organic chemistry. Such a combination will ensure capability in broad, creative approaches to building unprecedented, mixed inorganic/organic materials that have potential relevance to technological problems. Beyond the synthetic aspects, however, equal efforts are needed from analytical and physical chemists to provide quantitative analyses of the new structures and a detailed understanding of the formation mechanisms that lead to desired properties. The utility of the SAM will depend on some critical property. In many cases, these properties may be relatively complex such as an optoelectronic or biological response or an influence on corrosion or wear. The cooperation of other experts such as materials scientists, physicists, electrical and mechanical engineers, or biologists would be of obvious help. Although there is no question that critical advances in this technology can be made by individual specialists, we highly recommend that multidisciplinary efforts be encouraged to provide novel and creative approaches.

There are clear instrumentation needs to support the tasks of quantitative chemical and structural analysis of these organized structures. The combination of subtle but critical structural features, sensitivity toward degradation, and the monolayer-level amounts of materials has resulted in the emergence of only a few dependable instrumental techniques for analysis in these systems (see characterization section). There is a need for further development of instrumentation to solve these difficult, nontraditional analytical problems, and such efforts should be encouraged. For existing instrumentation, there are two categories of issues: those dealing with independent investigator instrumentation and those dealing with multiuser facilities. The majority of analytical efforts will require laboratory-centered instrumentation, such as X-ray photoelectron spectroscopy (XPS), Fourier transform infrared spectroscopy (FTIRS),

60

and secondary ion mass spectrometry (SIMS). It is clear that the most advanced and meaningful studies of SAMs will require the use of this type of instrumentation on a regular basis. Some of the more recent and detailed analyses now include the use of national facilities, in particular, synchrotron sources for in-plane X-ray diffraction and near-edge X-ray fine structure spectroscopy. As the field moves to problems requiring imaging analysis, scanning Auger and static SIMS will become more important. Scanning tunneling microscopy (STM), atomic force microscopy (AFM), and related techniques such as near-field imaging are also increasingly valuable in characterizing local structure down to the atomic level. Brewster angle microscopy and high-sensitivity scanning electron microscopy (SEM) are becoming important techniques. Although only limited use of such facilities is needed, it is important that these facilities continue to be readily available to users working on the chemistry of organic films. The lack of additional facilities of this type, however, is not limiting the progress of research at this time.

B. Payoffs

Support of fundamental and applied research into SAMs will lead to energy savings through enhanced understanding of interfacial processes vital to almost every technology. These technologies are outlined.

1. Tribology

SAMs are already known to confer new friction and wear characteristics on substrates, in all cases improving wear resistance. Because the effects of SAMs on boundary-layer lubrication can be modeled computationally, such studies will enhance mechanistic studies and provide a basis for practical improvements.

2. Fuel Cells

SAMs can provide technology for surface modification that will improve the manufacturability and operation of fuel cells in several areas: improved adhesion and contacts between components with fewer defects and leaks; improved capability to control gas distribution to the electrode surfaces and water distribution at (or removal from) these surfaces; possibly improved overall performance of the cells as redox catalysts for the cathode, thus dramatically affecting energy costs.

3. PV Cells and EC Windows

SAMs may find applications as protective coatings or adhesion-promoting layers for both active and passive components of PV cells and EC windows. Chemisorbed monolayers having close-packed alkyl chains should decrease diffu-

sion rates of water to, and their condensation at, interfaces containing polycrystal-
line-active layers (e.g., CdTe), processes that are probably associated with failure
of almost all devices. These monolayer films might also increase device lifetimes
by stabilizing heterojunctions (e.g., CdTe [p]/CdS [n]) or "fingers" of metalliza-
tion. One of the most immediate benefits in this area may be in relating modes of
failure at critical device interfaces to their molecular and atomic compositions. The
potential applications of SAMs for the encapsulation of passive components such
as mirrors and solar collectors are discussed in the following section.

4. Surface Contamination: Soiling and Fouling

Interfacial contaminants can interfere with virtually every industrial unit
process, thereby increasing energy consumption, even if their concentration in
the bulk is very low. Systematic modification of surface properties — critical
surface tension, hydrogen-bonding capacity, polarity, dispersion-force energies,
and extent of fluorination — using SAMs will clarify the mechanisms by which
industrial streams contaminate equipment, thereby facilitating prevention. Heat-
transfer pipes are notoriously subject to fouling and clogging and should be given
top priority for antisoiling treatment with SAMs designed for high-temperature
stability.

5. Fouling in Membrane Separations

Distillation, an enormously energy-consumptive technology, still accounts for
95% of U.S. industrial separations. Almost all of these separations could be carried
out more efficiently, near ambient temperature and with much less waste of
products, using membrane technology (microfiltration, ultrafiltration, reverse os-
mosis, electrodialysis, etc.) or hybrids of membrane separations with other meth-
ods. Membrane fouling, which reduces efficiency and raises costs, has strongly
inhibited substitution of membrane separations for distillation. Fluorinated LB
monolayers can, in certain circumstances, virtually eliminate membrane fouling,
and fluorinated SAM should confer the same benefit. Further research and devel-
opment and lifetime testing are essential.

The National Research Council reported in 1983 that a critical need for
improved detection by sensors is improved membranes for selective transport
between source and sensor. A nonfouling membrane is also necessary for this
application in any real environment.

6. Selectivity in Membrane Separations

The polymeric and ceramic membranes now commercially available each have
wide ranges of both pore size and selectivity. Selectivity in these systems depends
on the pore diameters and the physico-chemical interactions between the mem-
brane and feed stream. The only exceptions to the problem of nonuniform pore size

62

are "drilled" polycarbonate membranes, which have regular pores with nearly zero taper, but these membranes are inapplicable for many separations because of their large pore diameters. SAMs provide the means for healing the surface defects that account for much nonselective flux through standard membranes, adjusting pore sizes by deposition of films within pores, modifying the surface wettability of membranes to optimize separations, and adjusting the surface chemistry of membranes to optimize interactions with given feed streams.

Membranes with optimized selectivity are needed to provide chemically selective sensors and detectors. A related application of membranes anisotropically treated with SAMs is done in protective suits that do not allow diffusion of pesticides, pollutants, and chemical-warfare agents yet still allow the diffusion of moisture and CO_2 and the conduction of heat. This type of selectivity has been demonstrated, in fact, using LB films.

7. Biosurfaces

Natural cell membranes are OMAs with a minimal tendency to agglomerate proteins or cause other deleterious physiological reactions. Synthetic OMAs (e.g., those comprising organized phospholipids or derivatives thereof) have the potential for mimicking the characteristics of natural cells for *in vivo* applications without introducing materials that would be recognized as foreign. SAMs composed of these materials, therefore, offer great potential for coating prosthetic devices and implants as well as for optimizing the biocompatability of hemodialysis membranes and the surfaces in devices such as heart-lung machines.[14,15]

Biofouling is an important problem in a very broad range of technologies — marine corrosion due to anaerobic archaebacteria, corrosion of buried power cables, contamination of heat-transfer surfaces in cooling towers that cause a decrease in thermal efficiency, and decreased efficiency in ship transportation due to marine growth on hulls. SA organic structures will certainly be the best systems with which to determine the fundamental molecular processes underlying these types of fouling, and the results will aid in the design of improved systems (e.g., engineered polymer coatings) for their control. In certain circumstances, SAMs themselves may be solutions to the problems. For example, appropriate additives in cooling towers or heat exchangers may provide optimal strategies for controlling biofouling in these systems. Inclusion of SAM-forming components in polymers in a way that would permit them to "bloom" to the surface might be effective in preventing microbial adhesion and formation of slime layers.

8. Sensors

SAMs, by virtue of the flexibility with which they can be modified, provide the basis for technology that will introduce sensor molecules into appropriate sys-

tems.[16] For example, SAMs have already been built into small-area (ca. 1 μm^2) sensors for pH and ion-concentration measurement.[17,18] SAMs involving immobilized antibodies are the basis of a highly promising new technology using surface plasmon spectroscopy to carry out biospecific detection.[19,20] The recently developed method for attaching SAMs directly to the bare surface of GaAs suggests possibilities for developing new classes of chemical-sensing, semiconductor devices.[11] For a range of sophisticated environmental sensors of interest to DOE, SAMs will probably provide the best technology for introducing molecular recognition capability in optical and electrochemical systems.

9. Corrosion

Corrosion inhibition is an area in which SAMs have traditionally played an important role, although it has not always been recognized as such. Long alkyl chains, for example, form excellent barriers to H$_2$O, O$_2$, and various other corrosive agents. A better understanding of the principles underlying this phenomenon should lead to the rational design of SAMs for applications in corrosion inhibition involving a wide variety of both metals and semiconductors. SAMs could also be useful in coupling chemically labile substrates (e.g., copper) and chemically resistant layers (e.g., a micron layer of polymer), a strategy that would increase the mechanical durability of the interface.

REFERENCES

1. G. M. Whitesides and P. E. Laibinis, Wet Chemical Approaches to the Characterization of Organic Surfaces: Self-Assembled Monolayers, Wetting, and the Physical Organic Chemistry of the Solid-Liquid Interface, Langmuir, 6, 87 (1990); A. Ulman, An Introduction to Ultrathin Organic Films: From Langmuir Blodgett to Self-Assembly, Academic, New York, NY, 1991.
2. J. D. Swalen, D. L. Allara, J. D. Andrade, E. A. Chandross, S. Garoff, J. Israelachvili, T. J. McCarthy, R. Murray, R. F. Pease, J. F. Rabolt, and K. J. Wynne, Molecular Monolayers and Films, Langmuir, 3, 932 (1987).
3. J. D. Swalen, Optical Properties of Langmuir-Blodgett Films, J. Molec. Electronics, 2, 155 (1986).
4. N. Tillman, A. Ulman, and T. L. Penner, Formation of Multilayers by Self-Assembly, Langmuir, 5, 101 (1989); H. Lee, L. J. Kepley, H.-G. Hong, and T. E. Mallouk, Inorganic Analogues of Langmuir-Blodgett Films: Adsorption of Ordered Zirconium 1,10-Decanebisphosphonate Multilayers on Silicon Surfaces, J. Am. Chem. Soc. 110, 618 (1989); S. D. Evans, A. Ulman, K. E. Gopert-Berrarducci, and L. J. Gerenser, Self-Assembled Multilayers of Mercaptoalkanoic Acids: Selective Ionic Interactions, J. Am. Chem. Soc., 113, 5866 (1991).
5. S. D. Evans and A. Ulman, Surface Potential Studies of Alkanethiol Monolayers on Gold, Chem. Phys. Lett., 170, 462 (1990); A. Ulman, S. D. Evans, Y. Shnidman, R. Sharma, and J. E. Eilers, Mixed Alkanethiol Monolayers on Gold Surfaces: Wetting and Stability Studies, Adv. Colloid Interface Sci., 39, 175 (1992).
6. L. Addadi and S. Weiner, Control and Design Principles in Biological Mineralization, Angew. Chem. Int. Ed. Eng., 31, 153 (1992).

7. C. S. Dulcey, J. H. Georger, Jr., V. Krauthaner, D. A. Stenger, T. L. Fare, and J. M. Calvert, Deep UV Photochemistry of Chemisorbed Monolayers: Patterned Coplanar Molecular Assemblies, Science, 252, 551 (1991).

8. D. Kang and M. S. Wrighton, Patterned Functionalization of Gold and Single Crystal Silicon via Photochemical Reaction of Surface-Confined Derivatives of (h⁵-C₅H₅)Mn(CO), Langmuir, 7, 2169 (1991); P. E. Laibinis, R. L. Graham, H. A. Biebuyck, and G. M. Whitesides, X-ray Damage to CF₃CO₂-Terminated Organic Monolayers on Si/Au Supports is Due Primarily to X-ray Induced Electrons, Science, 254, 981 (1991).

9. Z. F. Liu, K. Hashimoto, and A. Fujishima, Photoelectrochemical Information Storage Using an Azobenzene Derivative, Nature, 347, 658 (1990).

10. H. Ringsdorf, B. Schlarb, and J. Venzmer, Molecular Architecture and Function of Polymeric Oriented Systems: Models for the Study of Organization, Surface Recognition, and Dynamics of Biomembranes, Angew. Chem. Int. Ed. Engl., 27, 113 (1988); Molecular Self-Assembly and Nanochemistry: G. M. Whitesides, J. P. Mathias, and C. T. Seto, A Chemical Strategy for the Synthesis of Nanostructures, Science, 254, 1321 (1991).

11. C. W. Sheen, J.-X. Shi, J. Mårtensson, A. N. Parikh, and D. L. Allara, A New Class of Organized Self-Assembled Monolayers: Alkane Thiols on GaAs (100), J. Am. Chem. Soc., 114, 1514 (1992).

12. K. R. Stewart, G. M. Whitesides, H. P. Godfried, and I. F. Silvera, Improved Adhesion of Thin Conformal Organic Films to Metal Surfaces, Rev. Sci. Instrum., 57, 1381 (1986).

13. J. M. Stouffer and T. J. McCarthy, Polymer Monolayers Prepared by the Spontaneous Adsorption of Sulfur-Functionalized Polystyrene on Gold Surfaces, Macromolecules, 21, 1204 (1988).

14. W. Fabianowski, L. C. Coyle, B. A. Weber, R. D. Granata, D. G. Castner; A. Sadownik, and S. L. Regen, Spontaneous Assembly of Phosphatidylcholine Monolayers via Chemisorption onto Gold, Langmuir, 5, 35 (1989).

15. E. S. Simon, K. L. Prime, and G. M. Whitesides, Formation of Self-Assembled Monolayers by Chemisorption of Derivatives of Oligo(ethylene glycol) of Structure HS(CH₂)₁₁(OCH₂CH₂)ₘOH on Gold, C. Pale-Grosdemange, J. Am. Chem. Soc., 113, 12 (1991); K. L. Prime, and G. M. Whitesides, Self-Assembled Organic Monolayers: Model Systems for Studying Adsorption of Proteins at Surfaces, Science, 252, 1164 (1991).

16. I. Rubinstein, S. Steinberg, Y. Tor, A. Shanzer, and J. Sagiv, Ionic Recognition and Selective Response in Self-Assembling Monolayer Membranes on Electrodes, Nature, 332, 426 (1988); E. Sabatani, I. Rubinstein, R. Maoz, and J. Sagiv, Organized Self-Assembling Monolayers on Electrodes Part I. Octadecyl Derivatives on Gold, J. Electroanal. Chem., 219, 365 (1987).

17. J. J. Hickman, D. Ofer, P. E. Laibinis, G. M. Whitesides, and M. S. Wrighton, Molecular Self-Assembly of Two-Terminal, Voltametric Microsensor with Interna References, Science., 252, 688 (1991).

18. J. J. Hickman, D. Ofer, C. Zou, M. S. Wrighton, P. E. Laibinis, and G. M. Whitesides, Selective Functionalization of Gold Microstructures with Ferrocenyl Derivatives via Reaction with Thiols or Disulfides: Characterization by Electrochemistry and Auger Electron Spectroscopy, J. Am. Chem. Soc., 113, 1128 (1991).

19. L. Häussling, H. Ringsdorf, F.-J. Schmitt, and W. Knoll, Biotin-Functionalized Self-Assembled Monolayers on Gold: Surface Plasmon Optical Studies of Specific Recognition Reactions, Langmuir, 7, 1837 (1991).

20. M. J. Tarlov and E. F. Bowden, Electron Transfer Reaction of Cytochrome c Adsorbed on Carboxylic Acid Terminated Alkanethiol Monolayer Electrodes, J. Am. Chem. Soc., 113, 1847 (1991); T. Sagara, K. Niwa, A. Sone, C. Hinnen, and K. Niki, Redox Reaction Mechanism of Cytochrome c at Modified Gold Electrodes, Langmuir, 6, 254 (1990).