LANGMUIR–BLODGETT FILMS

Thin organic films deposited on solids from the surface of water may have applications in technologies ranging from molecular electronics and microelectronics to integrated optics and microlithography.

Vijendra K. Agarwal

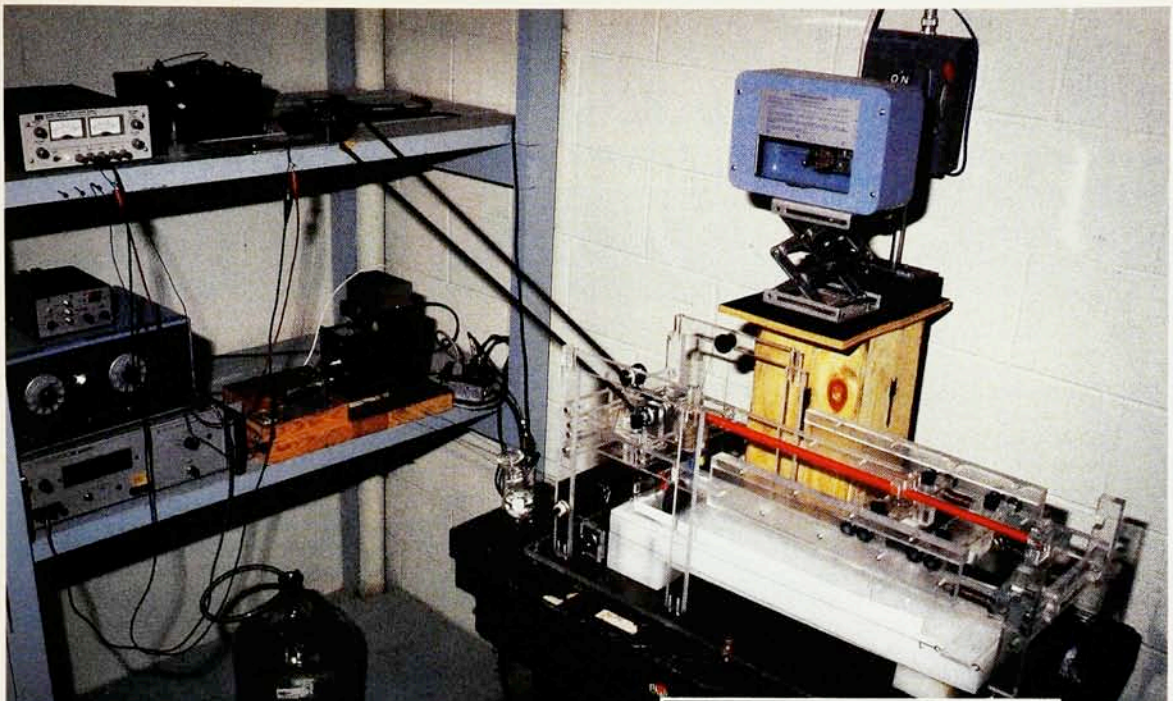
The science and technology of thin films have advanced so rapidly in recent years that investigators are now specializing, responding to the growing need to understand the properties of films of various compositions and thicknesses. Of particular scientific and technological promise are organic thin films grown by the classical dipping technique developed during the period 1917–35 by Irving Langmuir and Katharine Blodgett. By building multilayer films on solid surfaces from monolayer films on water, investigators are now developing and studying innovative materials with a wide range of potential technological applications, including molecular electronics, microelectronics, integrated optics and microlithography. Inorganic thin films of materials such as silicon dioxide have made possible the very-large-scale integration of electronic circuits. If the device geometries in these circuits shrink to nanometer dimensions over the next several decades, as some expect, Langmuir–Blodgett films with nanometer dimensions and a high degree of structural order will be of special importance.

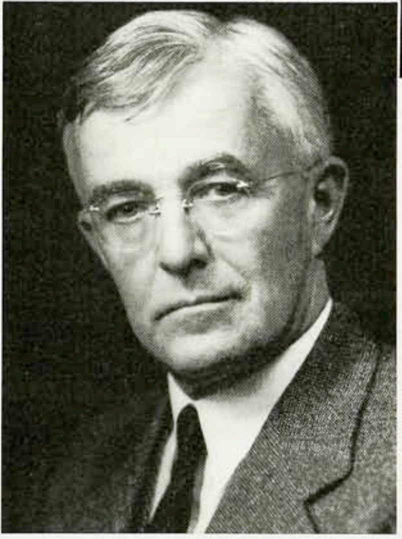
Some enthusiasts speculate that both passive and active components of devices, which are traditionally fabricated with inorganic materials, can be replaced by organic films. Here a word of caution is in order, as most organic films are fragile. On the other hand, recent work on new organic materials and better instrumentation for preparing and characterizing films is likely to yield thin films with good mechanical integrity, thermal and chemical stability and desirable electrical properties. The main focus of this article is organic films prepared by the Langmuir–Blodgett technique. The technique has been called the organic analog of molecular-beam epitaxy, but may turn out to be a more powerful tool.

History

According to legend, the use of thin films dates back as far as the 18th century BC, when oil was used to calm rough waters. In the 18th century AD, Benjamin Franklin conducted a more scientific investigation of the calming effect of an oil film only a few nanometers thick and described his findings in a well-documented communication to the Royal Society in 1774. After a century of almost no activity, Lord Rayleigh, followed by Agnes Pockels, suggested that a film of oil on water is approximately one molecule thick. It was Langmuir, however, who fully appreciated and developed the theory of monolayers. Monomolecular films of organic materials at

Vijendra Agarwal is an associate professor of physics at Moorhead State University, in Moorhead, Minnesota. He is currently on leave from Texas Tech University, in Lubbock, Texas.

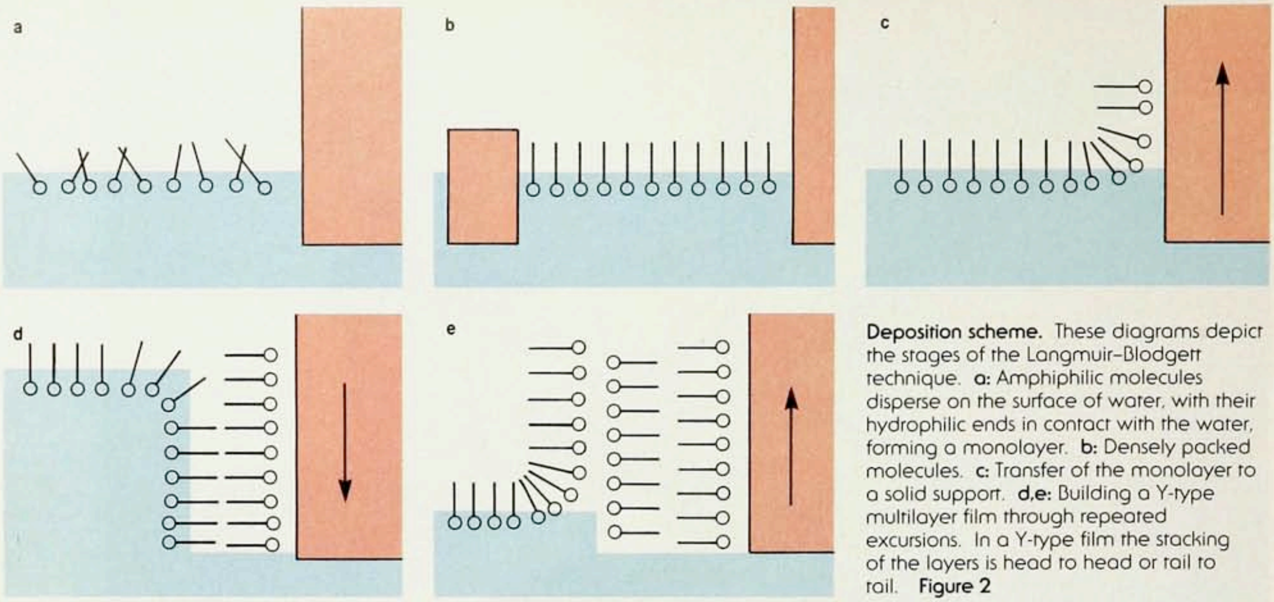




Langmuir–Blodgett trough. Right: Irving Langmuir (1881–1957) and Katharine Burr Blodgett (1898–1979). The trough, designed and built at Texas Tech University, maintains the surface density of a one-molecule-thick film on water as the film is deposited on the surface of a solid. The system monitors the film with a Wilhelmy-plate surface pressure sensor, which is connected to a feedback device that controls a constant-perimeter, variable-area barrier. Visible to the left of the trough are the dipping counter, gearbox, electric motors and the control system for the Wilhelmy balance. (Langmuir and Blodgett photographs courtesy of General Electric Research and Development Center.) **Figure 1**

an air–water interface are now known as Langmuir films. Langmuir was the first to explain the apparent discontinuities in plots of surface pressure versus area (isotherms) as phase transitions, and he was the first to determine the orientation of molecules at the air–water interface. This was followed by Langmuir and Blodgett's development of their classical dipping technique, which allows the transfer of monolayers from the surface of water onto solid substrates. These transferred monolayers are now referred to as Langmuir–Blodgett films.

A 16-mm movie made in 1939 and said to be part of the "Nobel Science Series" (even though it was the only one ever produced) shows a sequence of demonstrations by Langmuir himself—spreading camphor, motor oil and egg albumin on water and manipulating these monolayers rapidly and almost casually. Initially Langmuir had pursued monolayer studies to satisfy his own curiosity about molecular behavior on water. Later the work became the core of what we now know as surface chemistry, and Langmuir received the 1932 Nobel Prize in Chemistry for his contribution. In the same movie, Blodgett demonstrates the application of Langmuir–Blodgett films. She shows a voltmeter with part of its glass face coated with fatty-acid films, which work as an antireflective coating. Unfortunately the fragility of such films has prevented their commercial use as antireflective



Deposition scheme. These diagrams depict the stages of the Langmuir–Blodgett technique. **a:** Amphiphilic molecules disperse on the surface of water, with their hydrophilic ends in contact with the water, forming a monolayer. **b:** Densely packed molecules. **c:** Transfer of the monolayer to a solid support. **d,e:** Building a Y-type multilayer film through repeated excursions. In a Y-type film the stacking of the layers is head to head or tail to tail. **Figure 2**

coatings. Recently, interest in this application has revived because one can polymerize Langmuir–Blodgett films of various materials to provide mechanical rigidity and thermal stability. In fact, investigators now expect that polymerized Langmuir–Blodgett films may serve as a "two in one" product: coatings that are both protective and antireflective.

Following a period of active research on Langmuir–Blodgett films at General Electric Laboratories, World War II interrupted work on the films. In the 1960s the pioneering work of Hans Kuhn in West Germany on energy transfer in carefully constructed supermolecular structures revived interest in Langmuir–Blodgett films. However, the relatively poor quality of films made results difficult to reproduce, and this, coupled with the lack of development of new materials, kept work on Langmuir–Blodgett films moving at a slow pace. In recent years a concerted effort by physicists, chemists, biologists and device and materials scientists worldwide has increased the pace of research in this area. One of many measures of this rapid growth is that the third international conference on Langmuir–Blodgett films in July 1987 attracted almost twice the number of participants and contributed papers as the first such conference in 1982. The proceedings of these conferences and many other authoritative reviews provide comprehensive coverage of the scientific and technological potential of Langmuir–Blodgett films.[1–10]

Building multilayer films

The essential components of the apparatus for depositing Langmuir–Blodgett films are a trough filled to the brim with water, on which the monolayer floats, and a dipping device that moves the substrate up and down through the surface of the water. In the past decade the growing interest in characterizing and applying Langmuir–Blodgett films has led researchers to design many improved trough and control systems. One system for compressing the monolayer—to keep its surface pressure constant as it is taken up by the substrate—employs a trough whose perimeter remains constant but whose area changes as directed by a Wilhelmy-plate pressure sensor and feedback device. A Wilhelmy plate is a small piece of material that hangs from a sensitive electronic balance and penetrates the water surface; the reading on the balance is directly proportional to the surface tension.

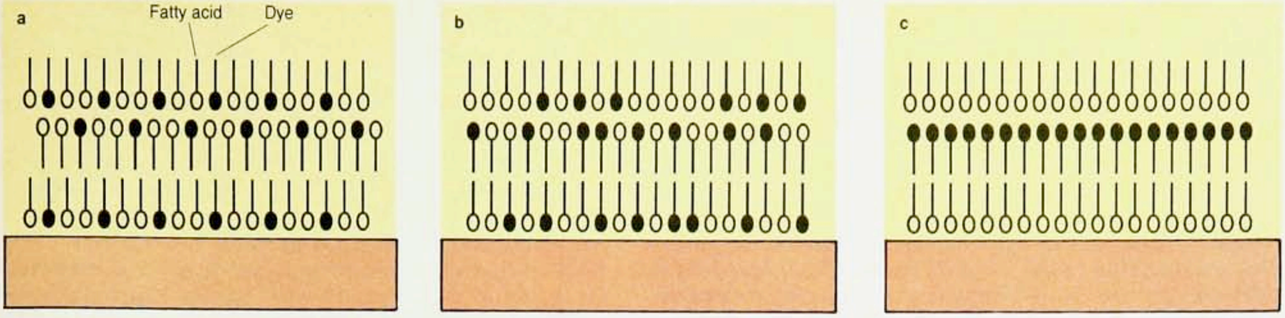
Figure 1 shows a similar system that we designed and constructed for our laboratory. The rectangular trough has a surface area of about 800 cm^2. It has a well that is 10 cm deep on the left end, where the substrate dips in, but only about 1 cm deep elsewhere. This allows considerable savings in the consumption of high-quality water. The framework, shaft, sprockets and chain are made of good-quality nylon or acrylic, and the bearings are greaseless stainless steel. A high-torque, low-speed dc motor drives sweeping barriers, which are narrow strips of glass or Teflon that move over the surface of the water to clean it at the beginning of each experiment. Another such motor drives the constant-perimeter barrier, which is a 3-cm-wide Teflon belt held in place by vertical glass rods. An ac motor with a multigear box drives the dipping mechanism.

A Kahn electrobalance (seen behind the trough in figure 1) with a 1-cm-wide Teflon Wilhelmy plate monitors the surface pressure. The system is semiautomatic and counts the number of up and down strokes of the substrate. The control system, Wilhelmy balance, electric motors, counter and gearbox are seen to the left of the trough in figure 1 and are isolated from the trough to avoid vibrations. The trough and framework are housed in a glove box (not shown) that sits on a 200-lb vibration-free granite table.

Commercial troughs are now available with sophisticated features. Alternate-layer Langmuir–Blodgett troughs, for example, allow deposition of monolayers of two materials, yielding structures of the form ABAB.... These structures show properties such as pyroelectricity and second-harmonic generation. Going beyond the commercial troughs, many laboratories have devised specialized systems with various levels of automation. In one system a canal-lock method allows the substrate to move from compartment to compartment through an interlock. To reduce cross-contamination between deposition compartments, this design uses a third, intermediate compartment containing a purging apparatus.[10]

From monolayer to multilayer

The first step in growing a Langmuir–Blodgett film is to spread a monolayer on a water surface. This requires amphiphilic molecules—that is, molecules with polar ends and nonpolar chains, which are hydrophilic and hydropho-



Molecular arrangements in two-component films. **a:** Fatty acid and dye molecules arranged periodically within each monolayer. **b:** No periodicity. **c:** Alternate layers of fatty acid and dye in a structure of the form ABAB. . . . **Figure 3**

bic, respectively. Fatty acids, which are hydrocarbon chains with polar ends, and the metal salts of fatty acids are classic amphiphilic organic materials. Stearic acid, $C_{17}H_{35}COOH$, is one such material. Typically, a drop of this material, dissolved in a solvent such as hexane, is put on a clean surface of water. The solvent evaporates, and the stearic acid spreads as a monolayer with the hydrophilic molecular ends in contact with the water and the hydrophobic chains almost upright, as figure 2a indicates. If one now compresses the monolayer to the extent that the surface pressure exceeds the equilibrium spreading pressure but remains below the "collapse" pressure, the molecules on the surface get squeezed into a vertical orientation, as in figure 2b.

The next step is to transfer monolayers from the water surface onto a solid support by dipping the solid in and out of the water. Under appropriate conditions, the solid picks up a monolayer on each excursion. On a hydrophilic substrate such as glass, however, the film will not deposit on the first downstroke; as figure 2c illustrates, glass picks up its first monolayer on an upstroke. Figures 2d and 2e show how the monolayers stack up on subsequent strokes to produce bilayers with the hydrophobic parts in the middle. Because deposition removes molecules from the monolayer on the water, one must reduce the area of the monolayer to maintain the surface pressure as multilayer deposition proceeds. With some materials, the Langmuir–Blodgett technique can stack as many as a thousand monolayers.

The head-to-head and tail-to-tail mode of stacking shown in figure 2 is the most common; a multilayer film constructed in this way is known as a Y-type film. There are two other modes of deposition: X-type, with all heads up, and Z-type, with all heads down. The mode of stacking depends on conditions of deposition such as temperature, surface pressure, speed of dipping and withdrawal, and pH and composition of the aqueous solution. There is considerable interest in X- and Z-type films, about which little is known because they are usually not very stable.

Multicomponent films

Langmuir demonstrated that if two substances each can spread as a monolayer on water, then they can be mixed in a single monolayer. It had to wait for the early 1960s, however, for Kuhn at the Max Planck Institute in Göttingen to pioneer the concept of using a molecular assembly technique to make mixed monolayers—of dyes and fatty acids, for example. Depending on the mixing ratio of the two components, the monolayers can be stacked with or without periodic arrangement of the component molecules, as figures 3a and 3b indicate, respectively. In recent years, Michio Sugi and his colleagues at Electrotechnical Laboratory in Japan have exploited the concept of mixed monolayers to form supermolecular structures. For example, Langmuir–Blodgett films containing chromophores at constant spacing in a plane with one-dimensional periodicity may serve as a model for photosensitive biological systems.[11] Consequently, there has been considerable activity in photoconduction studies of such systems.

Another important advance is the use of the Langmuir–Blodgett technique to build films with different materials in alternate layers, as figure 3c indicates. This is an elegant way to produce noncentrosymmetric structures of the form ABAB . . . , with the molecules in layers A and B at well-defined positions. Several research groups have recently designed troughs in which two monolayers are separated by a barrier. The substrate dips through one monolayer, picking it up, and then passes beneath the barrier and picks up the second monolayer as it emerges from the water. These developments open up a host of possibilities for "molecular architecure" and provide the basis for the use of Langmuir–Blodgett films in the production of systems with high optical nonlinearities.

Materials innovation

Most investigations involving the Langmuir–Blodgett technique use fatty acids or their metal salts. While films of these materials are very good insulators and are good model systems, their fragility and poor thermal stability are likely to render them unsuitable for many applications. Innovative chemists have cleverly devised a number of amphiphilic organic materials that can form Langmuir–Blodgett films the way fatty acids do, but that have the additional feature of polymerizability. Typical examples are vinyl stearate, ω-tricosenoic acid and diacetylenic acid, which polymerize under irradiation with cobalt-60 gamma rays, electrons and ultraviolet light, respectively, as figure 4 indicates. Experiments have also succeeded in incorporating anthracene and other polycyclic aromatic structures into Langmuir–Blodgett films, yielding materials with interesting electrical and optical properties.

Scientists have attempted to produce ultrathin Langmuir–Blodgett films of polyimide, starting from long-chain alkylamine salts. Such films are expected to be thermally stable up to about 400 °C, which would make them the most stable organic thin films yet known. Research aimed at producing wholly aromatic Langmuir–Blodgett films is also under way. Investigators have synthesized TCNQ-based organic materials that can be deposited with the Langmuir–Blodgett technique. (TCNQ is tetracyanoquinodimethane.) The resulting ultrathin conducting films have no external doping and exhibit very anisotropic conductivities—about 0.01 siemens per centimeter in the lateral direction in the metallic region. Such innovation should provide an additional stimulus in molecular electronics, making possible new field-effect transistor devices, for example. A great deal of research has focused on synthesizing surface-active dyes that can be deposited as Langmuir–Blodgett films. This work aims to unravel mysteries about the generation, injection and transport of photocarriers in molecular systems.

Fundamental properties

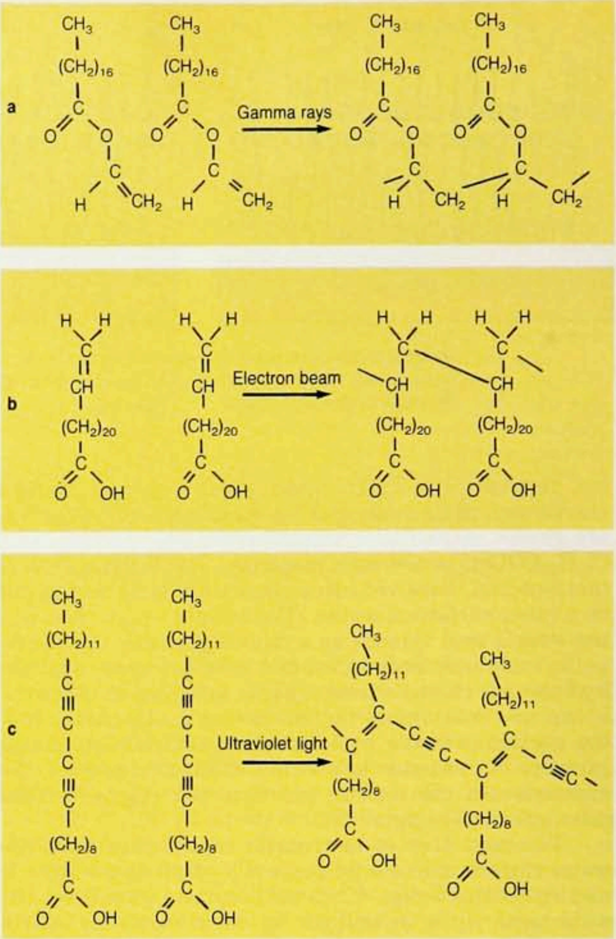
There is a wealth of information on the basic optical, spectroscopic and electrical properties of Langmuir–Blodgett films. One of the promising features of Langmuir–Blodgett film technology is the control it offers over the thickness of the layers in multilayer films. Figure 5 shows three independently measured parameters plotted as a function of the number of monolayers: the absorption from infrared reflection studies, the count rate of beta rays from carbon-14 in autoradiographic studies, and the inverse capacitance per unit area.[5] These curves represent only a small sample of the data illustrating the uniformity and reproducibility of good-quality layer-by-layer film growth.

Among the many tools used to measure the fundamental characteristics of Langmuir–Blodgett films are ellipsometry, electron spin resonance, infrared dichroism, polarized resonance Raman spectroscopy, attenuated transmission reflection, high-energy and low-energy electron diffraction, x-ray and neutron diffraction, and coherent anti-Stokes Raman spectroscopy. Basic studies with these tools have stimulated researchers to investigate the potential for using Langmuir–Blodgett films in such areas as physical electronics and nonlinear optics.

Melvin Pomerantz and his coworkers at IBM have taken advantage of the two-dimensionality of Langmuir–Blodgett monolayers to conduct fundamental studies of magnetism. They have found that the magnetic interaction between manganese ions in Langmuir–Blodgett films of manganese stearate is slightly anisotropic, so that the Heisenberg model does not apply. Near 2 K, there is a transition to an ordered state that is predominantly antiferromagnetic but has a weak ferromagnetic component. (See PHYSICS TODAY, January 1981, page 20.)

While we have seen progress in the study of the fundamental properties and potential applications of Langmuir–Blodgett films on substrates, a recent report by a panel commissioned by the materials science division of the Department of Energy suggests that "our progress . . . has been hindered by a number of problems and a certain lack of understanding of key fundamental processes."[7] The panel suggested that attention be given to refining the tools used to characterize thin organic films, improving the stability of films, understanding and reducing defects and gaining a detailed knowledge of the in-plane ordering of molecules.

This list, however, is by no means exhaustive. In some areas of even greater significance we understand next to nothing: monolayers on various solutions, for example, and the deposition process itself. Research is also needed on the effects of the pH of the aqueous solution, the purity of the material being spread, the spreading solvent, the surface and finish of the substrate, the static and dynamic angles of contact between the substrate and the floating film, the velocity of the substrate during deposition, and temperature—depositions are often performed at "room temperature," which is subject to seasonal, daily and random variations. The intermolecular forces and the hydrodynamics and thermodynamics of deposition have received very little attention. Although the plots of surface pressure versus area—the isotherms—have been known to exhibit discontinuities suggesting phase transitions, it is only within the last year or so that we have seen reports of phase transitions based on physical evidence in the form of x-ray diffraction data from monolayers on water. Here too, much remains to be understood.



Polymerizable materials that can be spread on water and deposited on solids as Langmuir–Blodgett films. **a:** Vinyl stearate. **b:** ω-Tricosenoic acid. **c:** Diacetylenic acid. The structures of the materials are shown before and after polymerization, which is accomplished with gamma rays, electrons and ultraviolet light, as indicated. **Figure 4**

Potential applications

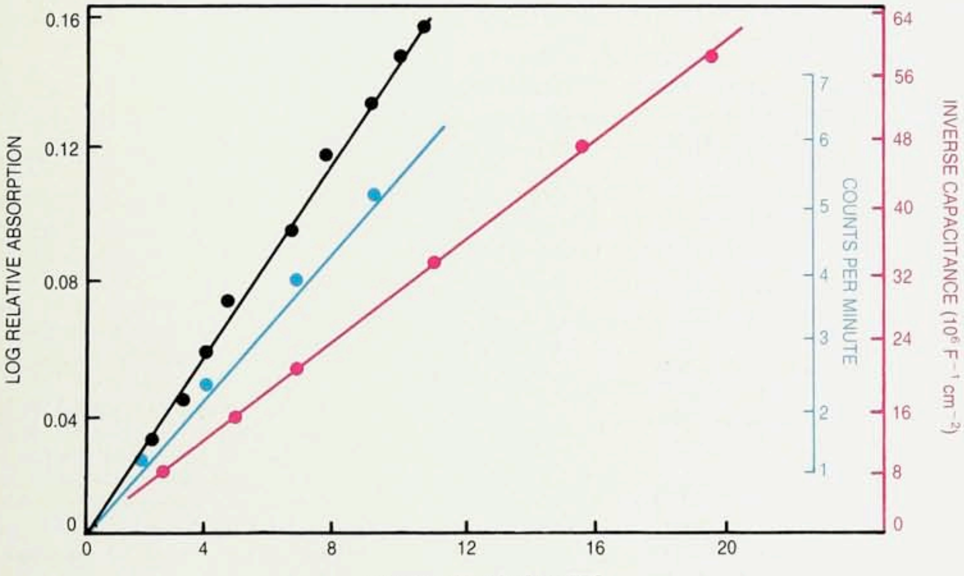
A few factors can be of overriding importance in applications of Langmuir–Blodgett films: control over the thickness of the film down to nanometers, the orientation and architecture of the molecules, and the uniformity of the film. Precise thickness control was important in the development of the "step gauge" at General Electric in

1937. The uses of films as tunneling spacers between electrodes and to form supermolecular structures for energy transfer studies were conceived of in the early 1960s. In recent years the availability of innovative film materials with much improved stability, together with better tools for deposition and characterization, has led to a number of interesting applications, which I discuss briefly below.

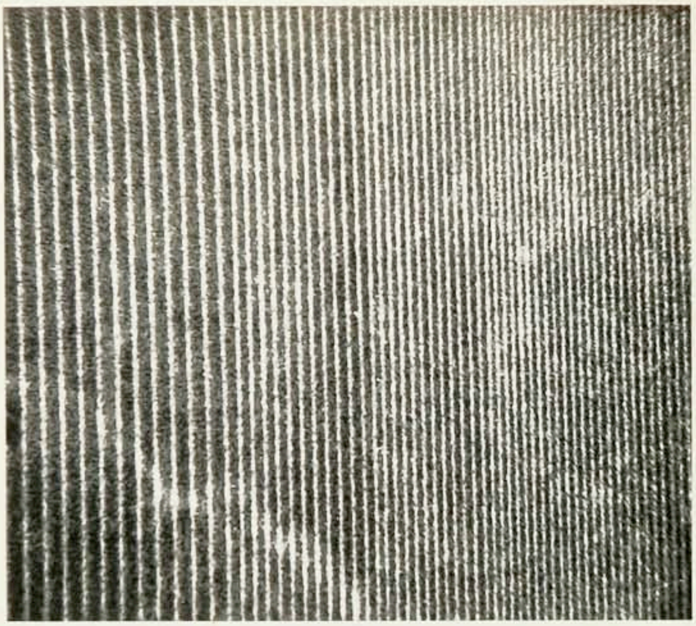
Nanometer-thick Langmuir–Blodgett films used as insulators on a host of semiconductor surfaces, among them Si, GaP, InP, CdTe and HgCdTe, have been shown to improve the characteristics of semiconductor devices such as photovoltaic cells. Gareth Roberts, now at Oxford University, and his coworkers at Durham University have pioneered work on using Langmuir–Blodgett films as insulators in metal–insulator–semiconductor devices. These MIS devices have since been used in developing selective and sensitive transducers, GaAs MISS switching devices and Josephson-effect devices. The use of phthalocyanine-based Langmuir–Blodgett films in field-effect semiconductor devices such as gas sensors has drawn particular attention. These sensors exhibit fairly high sensitivities to a variety of gases and have millisecond response times to gas concentrations of a few parts per million. Their recovery times are under 10 seconds—at least an order of magnitude shorter than those of devices based on evaporated films. In addition, investigators are exploring the possibility of using Langmuir–Blodgett films of valinomycin in ion-sensitive field-effect transistors.

Langmuir–Blodgett film technology is having an impact on microlithography due to the ever decreasing dimensions of integrated circuits. Experimenters have used Langmuir–Blodgett films as sensitive positive and negative resists in producing structures using ultrahigh-resolution electron beams. (See figure 6.) Langmuir–Blodgett films of fatty acid salts deposited on an amorphous carbon substrate about 20 nm thick act as an intrinsically positive resist—the molecules sublime when irradiated—with a resolution of 10 nm or better and a sensitivity of about 5 millicoulombs/cm^2. There are many negative resist materials, with films of ω-tricosenoic acid offering a particularly good compromise between resolution and sensitivity. French investigators at CEN Saclay have had varying degrees of success in making negative electron-beam resists out of a number of other materials that form Langmuir–Blodgett films. Much of the work aimed at producing new resists with improved resolution and sensitivity may be proprietary and thus beyond the public domain.

Electrically conducting polymers are technologically important, but progress on Langmuir–Blodgett films of these materials has been limited. Polydiacetylene, with its close resemblance to the well-known material polyacetylene, which is a good conductor when doped, should be a good choice for such studies. Langmuir–Blodgett films of polydiacetylene should have a softened crystal structure that allows greater penetration of dopants, leading to better electrical conductivities. Such a development would open up a host of challenging possibilities for building all-organic junction devices that would be analogous to conventional semiconductor devices. It may be possible to use films of fatty acids and doped and undoped



Linear dependences. Three characteristics of Langmuir–Blodgett fatty-acid films were measured independently and plotted as a function of the number of monolayers: absorption from infrared reflection studies (black line), count rate of beta rays from carbon-14 in autoradiographic studies (blue) and inverse capacitance per unit area (red). (Adapted from reference 5.) **Figure 5**



Lines drawn with an electron beam on a Langmuir–Blodgett film. The film is made up of 138 monolayers of manganese stearate on a graphite substrate. The narrowest lines are about 20 nm apart. (Courtesy of Melvin Pomerantz, IBM.) **Figure 6**

conjugated polydiacetylene to design organic superlattices with physical and chemical properties different from those of their constituents. Substrates made of single crystals of polydiacetylene would have minimal lattice mismatch in such periodic structures. The confinement of electrons or holes to selected layers of a Langmuir–Blodgett superlattice would enhance the two-dimensional mobility of these charges and have important ramifications for electrical conductivity.

The first demonstration that fatty acid films with a high degree of ordering and a low number of defects can guide optical waves was in the mid-1970s. Recent attempts have achieved much lower attenuations—less than 5 dB/cm—in such propagation, even in films of a stable polymer several hundred monolayers thick. More important than this linear optical response of Langmuir–Blodgett films, however, are nonlinear optical effects such as second- and third-harmonic generation. Interest in these effects is increasing because of their potential applications in signal, image and information processing and in probing surfaces and thin films. Studies of second-harmonic generation have focused on noncentrosymmetric Langmuir–Blodgett films of cyanine dyes, azo compounds and nitroamino compounds. Films of polydiacetylene have exhibited third-harmonic generation. Pyroelectric effects, piezoelectric effects and frequency doubling through second-harmonic generation are being sought in new amphiphilic compounds that form stable, polar, Z-type multilayered structures. Similar effects appear in Y-type films made of two materials. Coating optical fibers with nonlinear Langmuir–Blodgett films has increased the signal due to second-harmonic generation by as much as two orders of magnitude, a development that holds out the promise of frequency doublers, optical couplers and modulators fabricated on fibers.

Researchers outside of physics are also investigating and exploiting Langmuir–Blodgett films. Industrial chemists, for example, are taking an interest in using the films in adhesion and catalysis. Synthetic chemists are taking up the challenge of finding new materials that can be deposited as Langmuir–Blodgett films. Biologists are intrigued by the resemblance of lipid membranes to Langmuir–Blodgett bilayers, which may provide a basis for investigating the cooperative interactions among lipids in the membranes. Other bioscientists are interested in using Langmuir–Blodgett films as biosensors. Langmuir–Blodgett films may also be useful in display devices and in lubricating magnetic tape.

A field that began some 50 years ago with curiosity about the behavior of molecules on water has in the past decade helped bring us to the threshold of a new era of molecular science and engineering. As the editors of one volume on ultrathin films note, "The virtually limitless variety of organic molecules will allow for the design of molecules for specific properties and applications."[10] How well we take advantage of this opportunity will in large part depend on how closely physicists, chemists, biologists and electronic engineers work together.

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