back of any device. However, a judicious choice of the chemical medium may provide a material that would sustain a very large number of cycles. In addition, if the medium is kept at low temperatures (for example, in dry ice), side reactions are suppressed and fatigue may be minimized to a large extent; at low temperatures the persistence of the written form is extended considerably. Other molecules and matrices are possible candidates that could improve the speed, power consumption, and lifetime of the device.

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5 April 1989; accepted 28 June 1989

Orthogonal Self-Assembled Monolayers: Alkanethiols on Gold and Alkane Carboxylic Acids on Alumina

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This work demonstrates the practicality of forming two self-assembled monolayers (SAMs), independently but simultaneously, by adsorption of two different adsorbates from a common solution onto a substrate exposing two different materials at its surface. The experimental procedure and the degree of independence achieved in the resulting SAMs are illustrated by examination of monolayers obtained by adsorption of alkanethiols on gold and alkane carboxylic acids on alumina. This procedure provides a method for modifying the surface characteristics of microlithographically generated patterns and offers a versatile technique for controlling solid-vapor and solid-liquid interfacial properties in systems having patterns with dimensions of the order of 1 micrometer.

SELF-ASSEMBLED MONOLAYERS (SAMs) are highly ordered, quasi-two-dimensional structures formed by adsorption of appropriate precursors $X(CH_2)_nY$ from solution onto a solid substrate of metal or metal oxide (*1–5*). Techniques described to date for formation of SAMs offer very precise control over structure in the dimension perpendicular to the plane of the monolayer (*2*) but little control over structure or composition in the plane of the monolayer. For studies in wetting (*3*) and in microelectrochemistry (*6*, *7*), we also wanted to be able to control structure and to form patterns in the plane of the monolayer. We describe a technique that combines the formation of SAMs with the microlithographic preparation of substrates for them having two or more materials exposed at their surface. This technique provides control over in-plane surface properties and structure at the scale of the dimensions reached by the microlithographically generated features.

We take advantage of systems of adsorbants (A_1, A_2, . . .) and substrates (S_1, S_2, . . .) that are "orthogonal" in formation of SAMs: that is, A_i adsorbs strongly on S_i but weakly on S_j; A_j adsorbs strongly on S_j but weakly on S_i. A number of orthogonal systems can be imagined based on different principles of surface coordination chemistry. In this report we illustrate the application of orthogonal systems to the formation of in-plane patterns using "hard" and "soft" acid-base interactions (*8*) to differentiate between areas in the plane: $S_1 = Al_2O_3$, $A_1 = RCO_2H$; and $S_2 = Au$, $A_2 = R'SH$.

To demonstrate orthogonality in SAMs formed on the different substrates, a number of preliminary experiments were conducted with areas large enough for contact angle and x-ray photoelectron spectroscopy (XPS) measurements. In these experiments, substrates were prepared by evaporation of aluminum (∼500 Å) through a mask onto a gold substrate (*9*). On exposure of this patterned system to air, the surface of the aluminum oxidized spontaneously to aluminum oxide. Immersion of this substrate in an isooctane solution (*10*) containing an alkanethiol, $HS(CH_2)_mX$, and an alkane carboxylic acid, $HO_2C(CH_2)_nY$ (each ∼1 m*M*), for 24 hours resulted in adsorption of the thiol preferentially on the gold (*4*) and the carboxylic acid preferentially on the aluminum oxide (Fig. 1) (*5*). The composition of the SAMs formed on the gold and alumina were examined by XPS (*11*) (Fig. 2) and wettability (Table 1). The important conclusion from the data in Table 1 is that, within the limits of detection of our experiments, pure monolayers of the two adsorbates—$HS(CH_2)_mX$ on gold and $HO_2C(CH_2)_nY$ on alumina—are formed independently on the two types of exposed interfaces by ad-

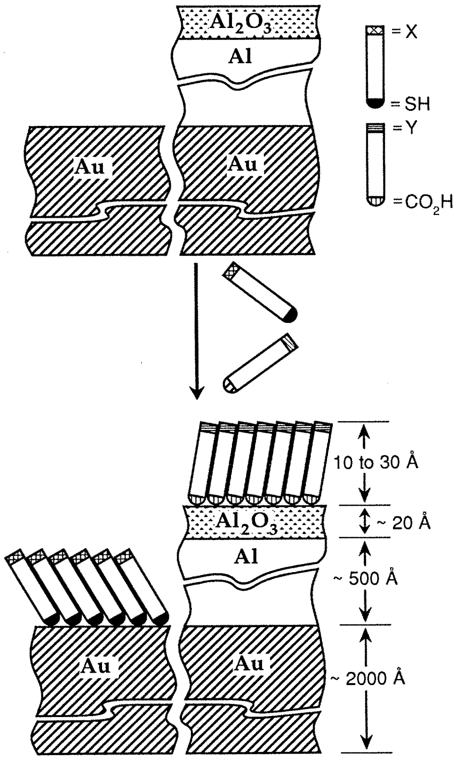

Fig. 1. Schematic illustration of the formation of orthogonal SAMs by adsorption of a mixture of alkanethiol [$HS(CH_2)_mX$] and alkyl carboxylic acid [$HO_2C(CH_2)_nY$] from a common solution onto a patterned gold–aluminum oxide surface.

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Table 1. Analysis of the organic monolayers formed by exposure of a substrate that has gold and alumina overlayers to a solution containing $HS(CH_2)_mX$ and $HO_2C(CH_2)_nY$. We estimate the threshold of detection of an XPS tag on the orthogonal surface (such as X on Al_2O_3 or Y on Au) to be 2 to 3% by mole for Br, ~1% by mole for Cl, and <0.5% by mole for F. The wetting data are advancing contact angles of water.

$HS(CH_2)_mX$		$HO_2C(CH_2)_nY$		Result
X	*m*	Y	*n*	
		XPS		
CH_3	17	Br	15	Br only on Al_2O_3
Br	11	CH_3	16	Br only on Au
CH_3	17	Cl	15	Cl only on Al_2O_3
Cl	11	CH_3	16	Cl only on Au
CH_3	17	$NHCOCF_3$	11	F only on Al_2O_3
$OCH_2C_2F_5$	11	CH_3	16	F only on Au
		Wetting		
OH*	11	CH_3	17	$\theta_a^{Au} < 15°$; $\theta_a^{Al_2O_3} = 96°$
CH_3	17	OH	15	$\theta_a^{Au} = 104°$; $\theta_a^{Al_2O_3} = 75°$

*Adsorption for this system was performed with anhydrous ethanol as the solvent.

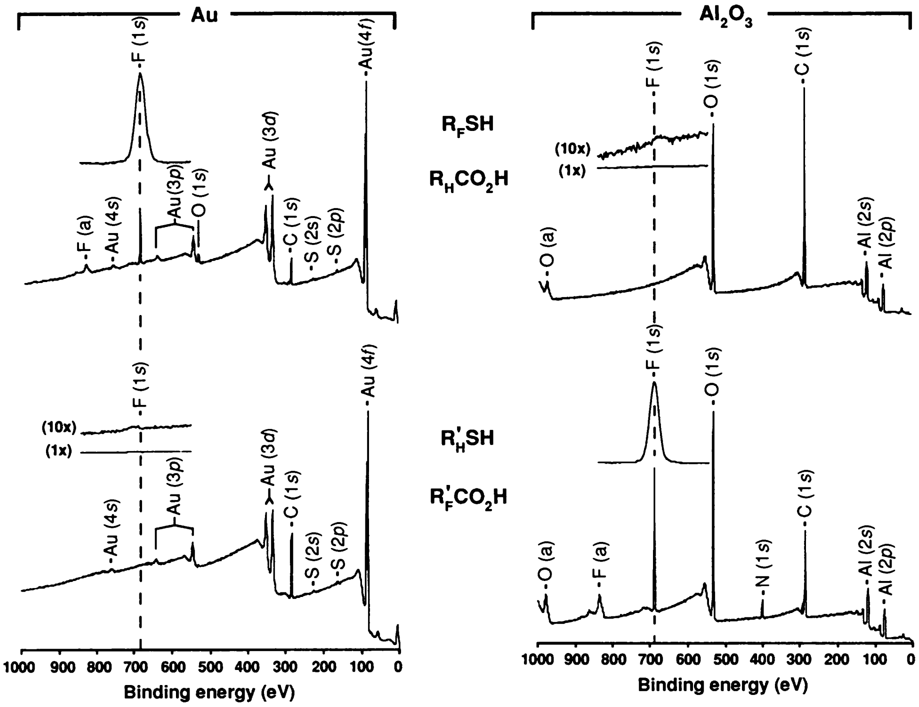

Fig. 2. XPS of SAMs formed from solutions containing mixtures of thiol and carboxylic acid on gold (left) and alumina (right); $R_FSH = CF_3CF_2CH_2O(CH_2)_{11}SH$, $R_HCO_2H = CH_3(CH_2)_{16}CO_2H$; and $R'_HSH = CH_3(CH_2)_{17}SH$, $R'_FCO_2H = CF_3CONH(CH_2)_{11}CO_2H$. Each sample is represented by a survey spectrum and by an insert showing the F(1*s*) region scanned from 680 to 700 eV at high resolution.

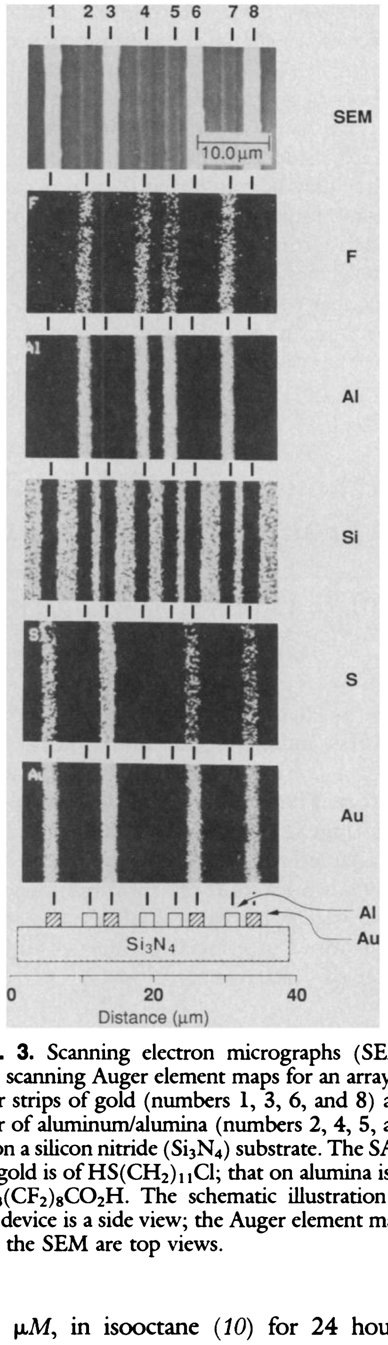

Fig. 3. Scanning electron micrographs (SEM) and scanning Auger element maps for an array of four strips of gold (numbers 1, 3, 6, and 8) and four of aluminum/alumina (numbers 2, 4, 5, and 7) on a silicon nitride (Si_3N_4) substrate. The SAM on gold is of $HS(CH_2)_{11}Cl$; that on alumina is of $CF_3(CF_2)_8CO_2H$. The schematic illustration of the device is a side view; the Auger element maps and the SEM are top views.

sorption from the same isooctane solution. Figure 2 shows XPS data for the system in which the sensitivity of XPS analysis is the highest (that based on detection of fluorine). The high degree of discrimination is clearly evident from the high-resolution spectra of the F(1*s*) region. The selectivity for binding is at least 100 to 1.

To demonstrate the formation of orthogonal SAMs at dimensions of greater interest in studying wetting and microelectrochemistry (≤1 μm), microelectrode arrays (*7*) were prepared on an insulating silicon nitride surface comprising eight wires—four gold and four aluminum. Each wire was ~2.4 μm wide, ~100 μm long, and ~1000 Å thick; the wires were separated by 1 to 2 μm. The array was cleaned by 30-min periods of sonication in sequence in hexanes, CH_2Cl_2 and CH_3OH, and was then exposed for 1 min to a flowing O_2 plasma (0.3 torr). The SAMs were formed by exposing the clean grid to a mixture of $CF_3(CF_2)_8CO_2H$ and $Cl(CH_2)_{11}SH$, each ~1 μ*M*, in isooctane (*10*) for 24 hours, which was then removed from solution and washed with hexanes. The device was grounded to a stage with silver paint and introduced into a scanning Auger microprobe spectrometer (*12*). Figure 3 shows a scanning electron micrograph and Auger element maps of the array. Beam damage to the derivatized array prohibited individual mapping of both halogen tags; sulfur, which proved to be less labile than chlorine, was mapped instead of chlorine. The maps establish that the fluorine is localized on the alumina, the sulfur on the gold, and that neither adsorbent is present on the silicon nitride. The selectivity inferred in these experiments is also at least 100 to 1.

The entries in Table 1 demonstrate the formation of several representative orthogonal SAMs. A large number of different organic functionalities should be compatible with this procedure. The last entry for Table 1 illustrates, however, one important current limitation of the technique. Although either hydrophobic or hydrophilic SAMs can be formed on gold, only hydrophobic SAMs can presently be formed on alumina: molecules $X(CH_2)_nY$ in which both X and Y are hydrophilic appear to adsorb with both polar functionalities bound at the alumina surface, and thus appear to form looped structures that are hydrophobic. This phenomenon occurs not only with alumina but seems to be common to metal oxides.

The technique of simultaneous formation of two different SAMs on a common, microlithographically prepared substrate exposing patterns of two different materials provides a new method for controlling and modifying the characteristics of surfaces. Since SAMs afford a high degree of control at the 2 Å scale perpendicular to the plane of the monolayer, and since lithography provides the ability to form lateral features having dimensions as small as 50 Å (*13*), the combination of the two offers a highly versatile protocol for the control of surface structure and properties.

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9. The gold substrate was prepared by evaporation of 100 Å of 99.99% chromium onto a polished Si(111) wafer followed by 2000 Å of 99.999% gold with the use of a cryogenically pumped E-beam evaporator operating at 10^{-6} torr.
10. For adsorbates only partially soluble in isooctane, substitution of anhydrous ethanol for isooctane yielded similar XPS and Auger results.
11. XPS spectra were obtained on a Surface Science Instruments spectrometer (Model SSX-100) operated at $<3 \times 10^{-9}$ torr with a 1-mm spot size.
12. Auger analysis was performed using a PHI 660 scanning Auger spectrometer operating at $<2 \times 10^{-9}$ torr. Mapping of SAMs proved to be extremely difficult at normal beam parameters. Although beam damage was minimized by using very low beam energies (0.5 to 3 nA, 8 to 15 kV), damage to some SAMs was so significant that element maps could only be obtained on the first pass.
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22 May 1989; accepted 30 June 1989

Evidence from Sediments of Long-Term *Acanthaster planci* Predation on Corals of the Great Barrier Reef

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Since 1962 the crown-of-thorns starfish, *Acanthaster planci*, has caused the devastation of living coral in large tracts of the Great Barrier Reef, Australia. Some authorities view this as a modern phenomenon, resulting from ecological disturbance caused by man. Evidence from skeletal remains in sediment suggests that large *A. planci* populations have been part of the Great Barrier Reef ecosystem for at least 8000 years. Coral predation by *A. planci* is likely to have influenced the morphological fabric of the Great Barrier Reef in its post-glacial development and may also have influenced species richness of the reef biota.

THE CROWN-OF-THORNS STARFISH (*Acanthaster planci* L.) is a major predator of hermatypic scleractinian corals, particularly in the western Pacific region (*1, 2*). Its population dynamics are considered to be cyclic (*3*) with low population densities alternating with dramatic population outbreaks that result in massive damage to the living coral cover of individual reefs and reef tracts (*4, 5*). The Great Barrier Reef has experienced two documented contemporary cycles, with outbreaks affecting reefs between Princess Charlotte Bay and the Swain Reefs Complex in the periods 1962 to 1977 and 1979 to 1986 (*6, 7*). It is thought that outbreaks occur first in the Cairns section of the Great Barrier Reef with reefs further south becoming progressively infested (*6*). Extensive regional surveys undertaken during 1985–86 indicated that, of 228 reefs surveyed in the Great Barrier Reef Province, approximately 27% had been affected by *A. planci* in the outbreaks of the present cycle (*7*).

The temporal context of the present crown-of-thorns predation cycles is a contentious issue. Some investigators argue that the cycles are a contemporary phenomenon directly attributable to interference by man in reefal ecosystems (*8*) thereby raising a major conservation issue in Australia and elsewhere. A converse view is that crown-of-thorn outbreaks represent an enduring ecological pattern that escaped notice until recently (*9*). The antiquity of *A. planci* outbreaks in the Great Barrier Reef is an important question to be answered.

Acanthaster planci contains a complex skeleton of small, arm-supporting ossicles and protective spines made of calcite. After death, these skeletal elements accumulate with reef sand as a recoverable fossil record. They are distinctive in color, shape, and microtexture and can be distinguished with certainty from other carbonate grains (*10*). Although the potential of this record in assessing the temporal distribution of *A.*

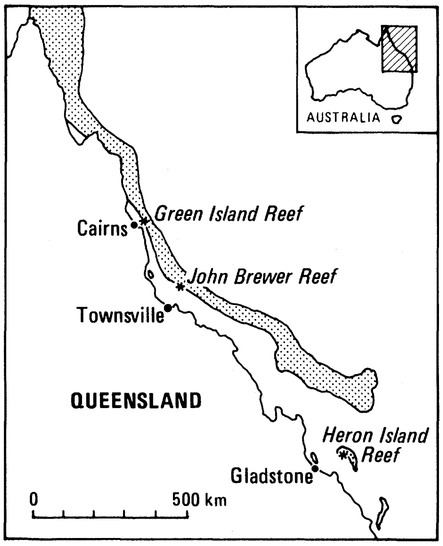

Fig. 1. Location of Great Barrier Reef sites examined for *A. planci* skeletal elements in the sediment record.

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