

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

PAUL E. LAIBINIS, JAMES J. HICKMAN, MARK S. WRIGHTON, AND GEORGE M. WHITESIDES\*

# 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.

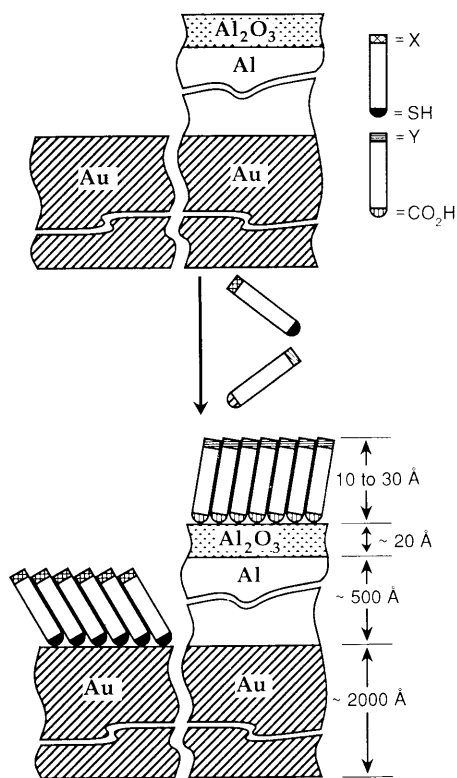
**S**ELF-ASSEMBLED MONOLAYERS (SAMs) are highly ordered, quasi-two-dimensional structures formed by adsorption of appropriate precursors  $X(\text{CH}_2)_nY$  from solution onto a solid substrate of metal or metal oxide (1–5). Techniques described to date for formation of SAMs offer very precise control 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 ( $A_1, A_2, \dots$ ) and substrates ( $S_1, S_2, \dots$ ) 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:  $S_1 = \text{Al}_2\text{O}_3$ ,  $A_1 = \text{RCO}_2\text{H}$ ; and  $S_2 = \text{Au}$ ,  $A_2 = \text{R}'\text{SH}$ .

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 ( $\sim 500 \text{ \AA}$ ) 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 isoctane solution (10) containing an

alkanethiol,  $\text{HS}(\text{CH}_2)_mX$ , and an alkane carboxylic acid,  $\text{HO}_2\text{C}(\text{CH}_2)_nY$  (each  $\sim 1 \text{ mM}$ ), 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— $\text{HS}(\text{CH}_2)_mX$  on gold and  $\text{HO}_2\text{C}(\text{CH}_2)_nY$  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 [ $\text{HS}(\text{CH}_2)_mX$ ] and alkyl carboxylic acid [ $\text{HO}_2\text{C}(\text{CH}_2)_nY$ ] from a common solution onto a patterned gold-aluminum oxide surface.

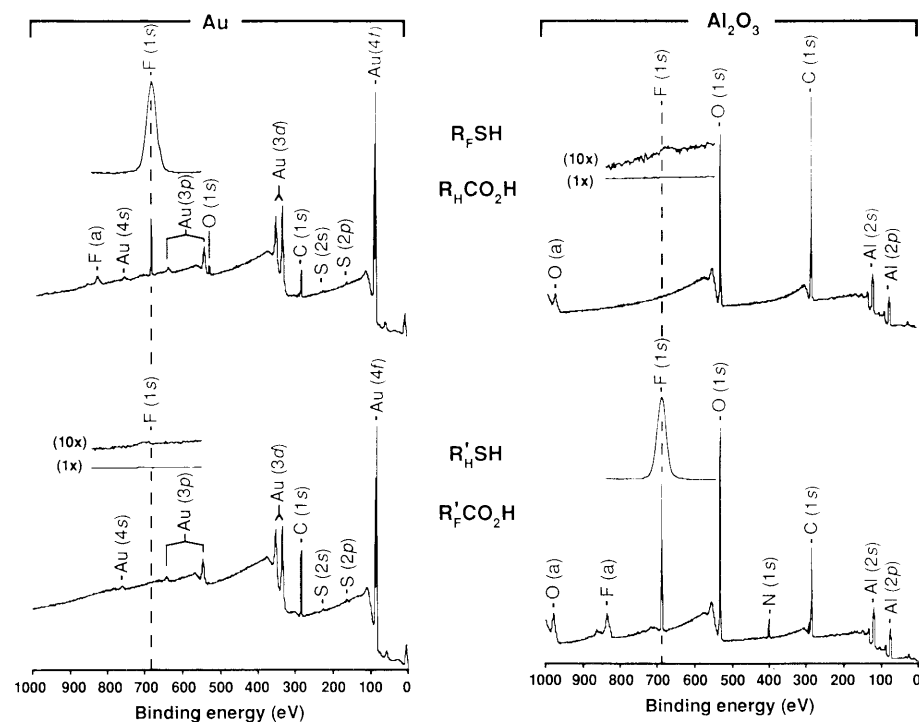
P. E. Laibinis and G. M. Whitesides, Department of Chemistry, Harvard University, Cambridge, MA 02138. J. J. Hickman and M. S. Wrighton, Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA 02139.

\*To whom correspondence should be addressed.

**Table 1.** Analysis of the organic monolayers formed by exposure of a substrate that has gold and alumina overlayers to a solution containing  $\text{HS}(\text{CH}_2)_m\text{X}$  and  $\text{HO}_2\text{C}(\text{CH}_2)_n\text{Y}$ . We estimate the threshold of detection of an XPS tag on the orthogonal surface (such as X on  $\text{Al}_2\text{O}_3$  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.

$\text{HS}(\text{CH}_2)_m\text{X}$		$\text{HO}_2\text{C}(\text{CH}_2)_n\text{Y}$		Result
X	m	Y	n	
XPS				
$\text{CH}_3$	17	Br	15	Br only on $\text{Al}_2\text{O}_3$
Br	11	$\text{CH}_3$	16	Br only on Au
$\text{CH}_3$	17	Cl	15	Cl only on $\text{Al}_2\text{O}_3$
Cl	11	$\text{CH}_3$	16	Cl only on Au
$\text{CH}_3$	17	$\text{NHCOCF}_3$	11	F only on $\text{Al}_2\text{O}_3$
$\text{OCH}_2\text{C}_2\text{F}_5$	11	$\text{CH}_3$	16	F only on Au
Wetting				
$\text{OH}^*$	11	$\text{CH}_3$	17	$\theta_a^{\text{Au}} < 15^\circ$ ; $\theta_a^{\text{Al}_2\text{O}_3} = 96^\circ$
$\text{CH}_3$	17	OH	15	$\theta_a^{\text{Au}} = 104^\circ$ ; $\theta_a^{\text{Al}_2\text{O}_3} = 75^\circ$

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

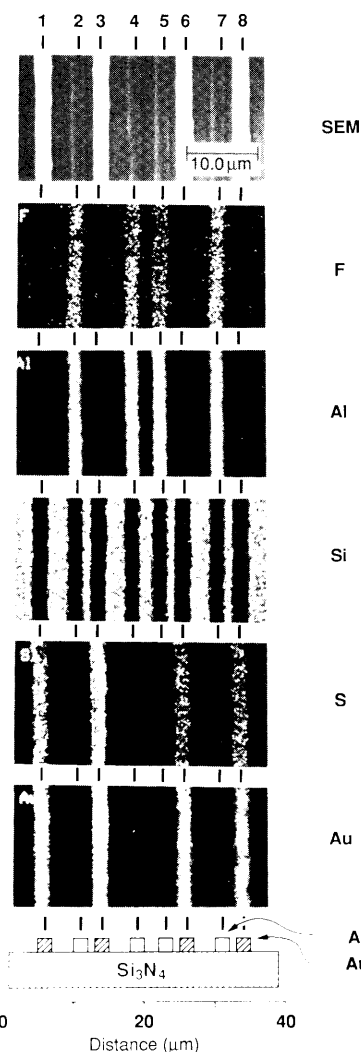


**Fig. 2.** XPS of SAMs formed from solutions containing mixtures of thiol and carboxylic acid on gold (left) and alumina (right);  $\text{R}_F\text{SH} = \text{CF}_3\text{CF}_2\text{CH}_2\text{O}(\text{CH}_2)_{11}\text{SH}$ ,  $\text{R}_H\text{CO}_2\text{H} = \text{CH}_3(\text{CH}_2)_{16}\text{CO}_2\text{H}$ ; and  $\text{R}'_H\text{SH} = \text{CH}_3(\text{CH}_2)_{17}\text{SH}$ ,  $\text{R}'_F\text{CO}_2\text{H} = \text{CF}_3\text{CONH}(\text{CH}_2)_{11}\text{CO}_2\text{H}$ . Each sample is represented by a survey spectrum and by an insert showing the  $\text{F}(1s)$  region scanned from 680 to 700 eV at high resolution.

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  $\text{F}(1s)$  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 ( $\leq 1 \mu\text{m}$ ), microelectrode arrays (7)

were prepared on an insulating silicon nitride surface comprising eight wires—four gold and four aluminum. Each wire was  $\sim 2.4 \mu\text{m}$  wide,  $\sim 100 \mu\text{m}$  long, and  $\sim 1000 \text{ \AA}$  thick; the wires were separated by 1 to 2  $\mu\text{m}$ . The array was cleaned by 30-min periods of sonication in sequence in hexanes,  $\text{CH}_2\text{Cl}_2$  and  $\text{CH}_3\text{OH}$ , and was then exposed for 1 min to a flowing  $\text{O}_2$  plasma (0.3 torr). The SAMs were formed by exposing the clean grid to a mixture of  $\text{CF}_3(\text{CF}_2)_8\text{CO}_2\text{H}$  and  $\text{Cl}(\text{CH}_2)_{11}\text{SH}$ , each



**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 ( $\text{Si}_3\text{N}_4$ ) substrate. The SAM on gold is of  $\text{HS}(\text{CH}_2)_{11}\text{Cl}$ ; that on alumina is of  $\text{CF}_3(\text{CF}_2)_8\text{CO}_2\text{H}$ . The schematic illustration of the device is a side view; the Auger element maps and the SEM are top views.

$\sim 1 \mu\text{M}$ , 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 ortho-

nal 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, microolithographically 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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14. We thank D. Ofer and M. Schloh for microlithogra-