Monolayers of 11-trichlorosilylundecyl thioacetate: A system that promotes adhesion between silicon dioxide and evaporated gold

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The use of sulfur-containing organic monolayer films improves adhesion between gold and silicon dioxide. The structures of these monolayers were analyzed using contact angle, ellipsometry, and XPS. The zone of adhesive failure was at or near the gold-monolayer interface.

I. INTRODUCTION

This article describes the use of sulfur-containing organic monolayers to improve the adhesion of gold to silicon substrates having a native silicon dioxide surface layer. Gold adheres to clean silicon,[1] but not to silicon dioxide.[2] The affinity of gold toward silicon dioxide can be improved by coating with chromium[3] or titanium[3] films or by adding interlayers containing fluoride salts.[4] Bombardment of gold-covered silicon dioxide with electrons[5] or heavy ions[6,7] also enhances adhesion. Thin (< 100 Å) covalently-bonded alkylsiloxane films containing amines or epoxides improve the adherence of gold to glass.[8]

Gold surfaces have a high affinity for alkyl thiols (RSH),[9,10] dialkyl sulfides (R_2S),[11,12] and dialkyl disulfides (RSSR).[13] The mechanisms of bonding between organic sulfur compounds and gold have not been clearly established, although surface gold thiolates have been suggested as important.[13,14] Allara and Nuzzo have exploited the affinity of gold for sulfur by using a relatively thick organic polysiloxane layer containing a disulfide to improve the adhesion of gold to alumina and silicon dioxide.[15,16]

We have shown previously that monolayers can be used to promote adhesion.[17] Here we demonstrate that covering a Si/SiO_2 substrate with a covalently attached organic monolayer film containing thiol groups (and possibly disulfides derived from them) or thioacetate groups improves the adhesion of gold to the substrate.

II. RESULTS

A. Preparation of monolayers

The molecular precursor to the desired monolayer was 11-trichlorosilylundecyl thioacetate, $Cl_3Si(CH_2)_{11}$-$SCOCH_3$, **1**. Scheme I outlines the synthesis of **1**. We protected the thiol group as a thioacetate to prevent reaction of free thiols with chlorosilane groups. Substrates for these experiments consisted of standard boron-doped semiconductor grade silicon wafers. These wafers were cleaned by heating in a mixture of 30% H_2O_2 and conc. H_2SO_4,[18] and stored under water until use.

$$\mathrm{CH_2=CH(CH_2)_9Br} \xrightarrow[\text{EtOH}]{\text{Na SCOCH}_3} \mathrm{CH_2=CH(CH_2)_9SCOCH_3} \quad 85\,\%$$

$$\xrightarrow[\text{cat. H}_2\text{PtCl}_6]{\text{HSiCl}_3} \mathrm{Cl_3SiCH_2(CH_2)_{10}SCOCH_3} \quad 56\,\%$$

Scheme I. Synthesis of 11-trichlorosilylundecyl thioacetate, **1**.

Figure 1 summarizes the preparation of the composite thin films. The thioacetate monolayers were assembled by immersing the wafers in freshly prepared solutions of **1** in methylene chloride.[19] We prepared control samples consisting of alkylsilane groups having no sulfur-containing functionality from hexadecyltrichlorosilane (HTS, $Cl_3Si(CH_2)_{15}CH_3$).[20] The thioacetate groups ($—SCOCH_3$) in monolayers derived from **1** were hydrolyzed to thiols (—SH) using hot conc. aqueous HCl (Fig. 1).[21]

B. Characterization of monolayers: Contact angle, ellipsometry, and x-ray photoelectron spectroscopy (XPS)

The advancing contact angle of water on monolayers derived from **1** was $\theta_a^{H_2O}$ = 78–80°; that for hexadecane (HD) was θ_a^{HD} = 0°. Hydrolysis of the ester and release of the thiol changed $\theta_a^{H_2O}$ only slightly to 72–74°. For comparison, $\theta_a^{H_2O}$ is ~ 70° for self-assembled monolayers of $HS(CH_2)_{12}SCOCH_3$ on gold.[10] No monolayer system has been prepared that presents a densely packed array of —SH groups. Experimental values for contact angles on such systems are thus not available.

Ellipsometric measurements indicated that the monolayers derived from **1** were 11–15 Å thick.[22] This value is less than the 20 Å that we would expect for a fully *trans*-extended alkyl chain oriented perpendicular to the Si/SiO_2 surface.[23] The structure of these monolayers probably corresponds to a fairly disordered liquid-like layer, rather than one that contains quasi-crystalline islands.[24] While the monolayers prepared from **1** were not close-packed structures, we demonstrate below that the effective density of thiol/disulfide groups was sufficient to achieve our goal of promoting adhesion to gold. On hydrolytic removal of the acetyl group, we observed a 0–2 Å decrease in the thickness of the monolayer (~2 Å would have been expected).[25] This change, while consistent with that expected

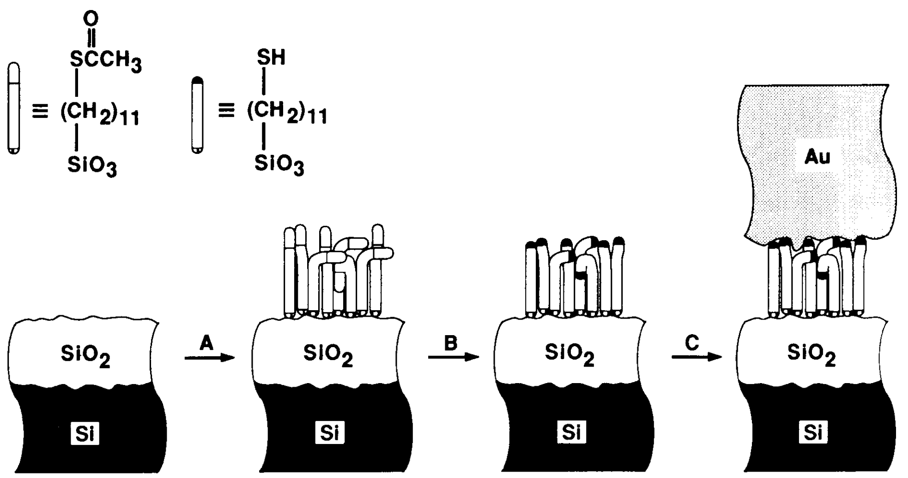


FIG. 1. Schematic representation of the preparation of the gold-silicon composite. (A) Formation of a thioacetate-terminated monolayer on Si/SiO_2 by reaction of $Cl_3Si(CH_2)_{11}SCOCH_3$ (**1**) in methylene chloride solution with Si–OH groups and adsorbed water on the surface of the substrate. (B) Formation of a thiol-terminated monolayer by acidic hydrolysis of the monolayer prepared in step A. (C) Thermal evaporation of gold (650–1000 Å) onto the thiol-terminated monolayer prepared in step B. The molecular order in these monolayer systems has not been defined, but the monolayers were thinner (and thus probably more disordered) than fully *trans*-extended chains oriented perpendicular to the surface.

for removal of an acetyl group, is small and is within the limits of uncertainty of the ellipsometric method.

The XPS spectra for these monolayers (Fig. 2) demonstrate that the elemental compositions of the monolayers were those expected. Survey spectra indicated the presence of only oxygen, silicon, carbon, and sulfur on the surface. Both the monolayer from **1** and that obtained from it by hydrolysis contained no chlorine: hydrolysis of the Si–Cl bonds was apparently complete. The monolayer from **1** showed a C 1*s* peak at 288.2 eV, corresponding to the carbonyl carbon of the $—SCOCH_3$ group. After hydrolysis in conc. aqueous HCl, the intensity of this peak had decreased to less than 20% of its original value. The S 2*s* electrons present in the monolayer before hydrolysis had a binding energy of 228.7 eV; after hydrolysis this energy had not changed significantly (< 0.3 eV).[26,27] The calculated atomic ratio of the C 1*s* (—SCO—) signal to that of sulfur in the unhydrolyzed monolayer was approximately 1.2:1. Although this ratio should be 1:1, these signals were weak and subject to significant quantitative error.

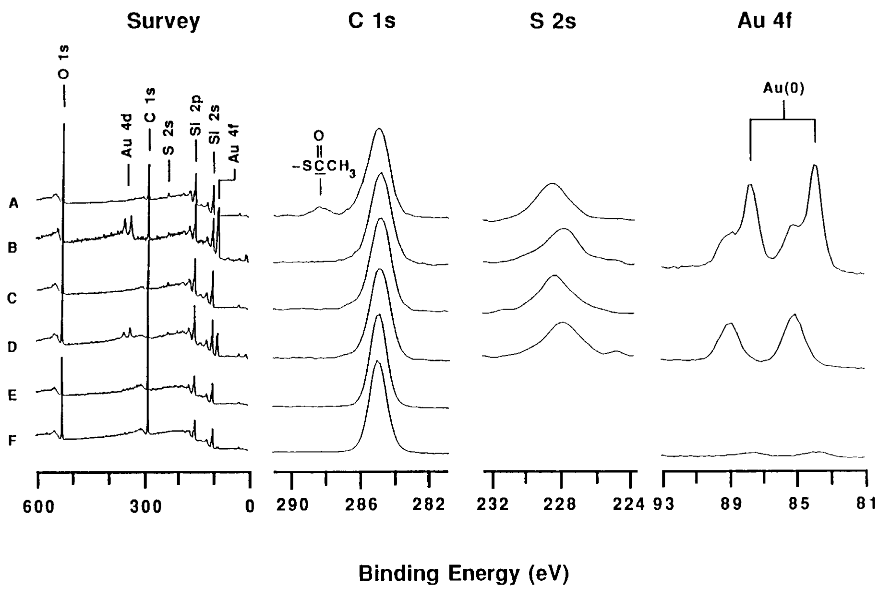


FIG. 2. XPS spectra of monolayers prepared from $Cl_3Si(CH_2)_{11}SCOCH_3$ (**1**) and $Cl_3Si(CH_2)_{15}CH_3$ (HTS) on Si/SiO_2 substrates: survey spectra (left) and high resolution spectra of the carbon 1*s* (left center), sulfur 2*s* (right center), and gold 4*f* (right) regions. Spectra are shown for these monolayers prior to evaporation of gold onto the sample (A, C, E) and for the monolayers that remained after the gold had been removed from the surface (B, D, F) (see text). Spectra are referenced to an average of the binding energies of the C 1*s*, Si 2*p*, and O 1*s* peaks. The C 1*s* and S 2*s* spectra are each normalized to the same maximum peak height. The Au 4*f* spectra are not normalized; their intensities represent the relative amounts of gold remaining on these surfaces. The S 2*s* spectra have been smoothed using a nine-point algorithm with a symmetrical triangle convolution function. (A. Savitzky, M. J. E. Golay, Anal. Chem. **36**, 1627 (1964).) (A) Thioacetate-terminated monolayer prepared from **1**. (B) A after removal of gold from the surface. The survey and Au 4*f* spectra include bulk gold (Au(0)) in the area surrounding the region of adhesive failure. (C) Thiol-terminated monolayer prepared by acidic hydrolysis (conc. HCl, 70 °C, 1.5 h) of A. (D) C after removal of gold from the surface. (E) Methyl-terminated monolayer prepared from HTS. (F) E after removal of gold from the surface.

The contact angle, ellipsometric, and XPS measurements imply that adsorption of **1** onto silicon substrates containing a surface oxide layer resulted in the formation of a loosely packed monolayer containing a terminal thioacetate. Upon acidic hydrolysis the protecting acetyl group was removed, resulting in a thiol- and/or disulfide-terminated interface. The contact angle and ellipsometric measurements on the thiol-terminated monolayer, as well as the continued presence of sulfur in the XPS spectrum, established that the monolayer was still bound to the surface after hydrolysis of the protecting group.

C. Preparation and characterization of gold-coated substrates

Gold layers (650–1000 Å) were formed by thermal evaporation onto four types of samples: bare Si/SiO_2 substrates and Si/SiO_2 having attached monolayers from **1** (containing —$SCOCH_3$ terminal groups), monolayers derived from **1** by hydrolysis (—SH and, perhaps, —SS— terminal groups), and monolayers from HTS (—CH_3 terminal groups). We evaluated the strength of adhesion of gold on these substrates semiquantitatively through peel tests using pressure sensitive tape (Table I). The tape was pressed into intimate contact with the gold overlayer and removed in a 180° test configuration at a rate of 1 mm/min. For both the bare Si/SiO_2 substrate and the substrate having a methyl-terminated monolayer, the strength of adhesion between the gold and the substrate was below our limits of detection. In the presence of both the —SH and —SAc-terminated monolayers, the adhesion strength was much greater. Adhesive failure on these samples occurred either at the interface between the tape and the gold or at the interface between the adhesive and the backing of the tape itself. No gold transferred to the tape; in some cases, visible residue from the adhesive in the tape remained on the gold surface. The adhesive strengths listed in Table I for these samples therefore are measurements of the strength of the gold-tape interface, rather than the apparently stronger gold-monolayer interface. At higher peel rates (100 mm/min) the sulfur-containing monolayers withstood forces of 400 g/cm.

TABLE I. Strength of gold-substrate interaction as a function of the chemical composition of the substrate surface.

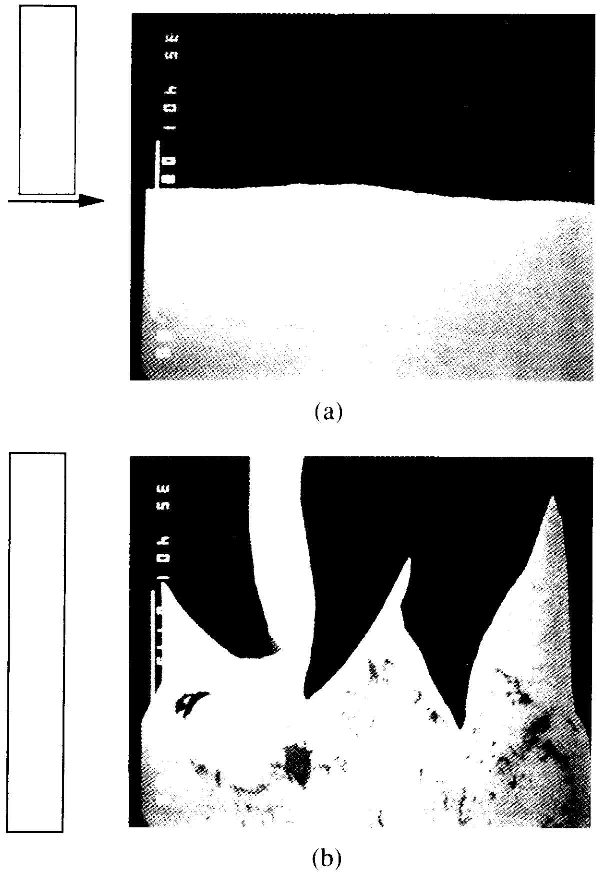
Surface composition[a]	Yield strength (g/cm)[b]
(1) —SH	> 84
(2) —$SCOCH_3$	> 70
(3) —CH_3	< 1
(4) SiO_2	< 1

[a] For the first three entries the interface in contact with the gold had the structure $Si/SiO_2/O_3Si(CH_2)_{11}R$, where R = —SH, —$SCOCH_3$, and —$(CH_2)_4CH_3$. The last entry is for Si/SiO_2 with no organic monolayer. The density of packing and the degree of order within these structures was probably $1 \approx 2 < 3$.

[b] For a peel test at 1 mm/min using pressure sensitive tape and a 180° test configuration.

While the interfaces between the gold and the sulfur-containing monolayers were strong enough to withstand these peel tests at low peel rates, we were occasionally able to cause failure in adhesion between the gold and the monolayer-coated substrate by pulling the tape rapidly by hand from the gold-covered surface. Failure under these conditions was not reproducible and we obtained surfaces after failure with drastically differing coverages of gold remaining on the substrate.[28]

Figure 3 presents scanning electron micrographs of the edge of the gold that remained on methyl- and thiol-terminated monolayers after adhesive failure. When peeling the tape from a methyl-terminated monolayer, all the



(a)

(b)

FIG. 3. Electron micrographs of the border of the gold remaining after adhesive failure. The light regions are gold; the dark areas correspond to the Si/SiO_2 substrate. The shaded region to the left of each micrograph indicates that part of the field of view which had been covered by the tape. The size markers in the micrographs correspond to 100 μm. (A) Methyl-terminated monolayer prepared from $Cl_3Si(CH_2)_{15}CH_3$ (HTS). The arrow indicates the approximate position and direction of the edge of the tape before its removal. The edge of the gold corresponds to the edge of the tape. (B) Thiol-terminated monolayer prepared by acidic hydrolysis (conc. HCl, 70 °C, 1.5 h) of a monolayer prepared from $Cl_3Si(CH_2)_{11}SCOCH_3$ (**1**). The entire field of view was covered by the tape. The edge of the gold represents the border of the region where failure in adhesion had occurred, but it does not correspond to the edge of the tape.

gold in the region covered by the tape was removed. This process also detached gold from regions adjoining that covered by the tape. The extension of the region from which the gold had been removed beyond the edge of the tape indicated that the cohesion within the gold leaf exceeded the adhesion of the gold to the monolayer. The edges of the gold that remained on this surface were relatively straight and no macroscopic (>10 μm) islands of gold were present in those areas previously covered by the metal overlayer.

When the tape was removed from a thiol-terminated monolayer, the total area of adhesive failure was significantly smaller than that observed for the methyl-terminated monolayer. In contrast to the latter surface, the zone of failure did not extend beyond the edge of the tape; that is, adhesion to the surface exceeded cohesion within the gold. The edges of the residual gold were irregular and islands of gold remained in the regions that had been under the tape.

Figure 2 also shows XPS spectra of those regions of the substrate from which the gold film had been removed for methyl-, thioacetate-, and thiol-terminated monolayers. These spectra were acquired in regions which did not contain any gold islands that were visible by optical microscopy at 50× magnification. (The spectra for the thioacetate-terminated monolayer include bulk gold surrounding the region of failure.) Comparisons of these spectra with those obtained before the substrates were covered with gold showed, in general, no major changes in the ratios of carbon, oxygen, silicon, and sulfur. The acetate group had, however, disappeared from the thioacetate-terminated monolayer. Virtually no gold remained on the methyl-terminated surface: the intensity of the Au $4f$ peak corresponded to trace quantities and the atomic ratio of gold to carbon was Au/C = 0.003. Similar quantities of residual gold were inferred for the bare Si/SiO_2 substrate. Almost ten times as much gold was retained on the surface of the sulfur-containing monolayers: Au/C = 0.03 and Au/S = 0.9–1.0.[29] These observations confirm the results of the peel tests: the presence of sulfur in the monolayer significantly increases the affinity of the surface for gold. We note that, after stripping the gold layer from the sulfur-containing monolayers, approximately one atom of gold was retained for each sulfur atom on the surface.

On the sulfur-containing interfaces, we observed a single species of gold whose binding energy was 0.80 ± 0.1 eV higher than that of Au(0) and that of the gold which remained on both the bare Si/SiO_2 substrates and the methyl-terminated monolayers.[30] The sulfur remaining on the thiol- and thioacetate-terminated interfaces after the gold had been removed had a binding energy 0.65 ± 0.1 eV lower than that of the sulfur in the original thioacetate.[31] These observations suggest that the residual gold on the thiol-terminated surface was in an oxidized form relative to Au(0) while the sulfur was somewhat reduced relative to that in the starting monolayer.[32] The observed shift in the binding energy could also be explained by changes in the size of gold clusters that remain on the monolayer. On poorly conducting substrates the Au $4f_{7/2}$ binding energy for coverages less than 2 monolayers shifts to higher binding energy.[33] This shift, whose magnitude increases (up to 0.6 eV) as the gold coverage decreases, has been attributed to the positive charge that remains after photoemission. We do not for two reasons believe that this effect is relevant to this study. First, our substrates were of low resistivity (0.5–40 Ω) and we did not observe any effects of differential charging. Second, the gold remaining on the thiol interface had a higher binding energy than that of the even lower amounts of gold left on the methyl surface.

III. DISCUSSION

Modification of the surface of a Si/SiO_2 substrate by covering it with a covalently bonded organic monolayer containing thiol groups significantly enhances the adhesion of evaporated gold to these substrates. Although this work clearly establishes that incorporation of covalently attached organosulfur compounds is a successful strategy for improving adhesion, our samples showed some variability from region to region. While we have not fully optimized the procedure nor identified the reasons underlying the variability in results, we offer two possible explanations for this irregularity. First, contamination of the sulfur-containing interface (probably by volatile organic compounds) may prevent interaction between the gold and the sulfur. Second, the strength of interaction between the sulfur and the evaporated gold may depend on the rate at which the gold is deposited. This rate could affect the degree of contact between the gold and the monolayer, the temperature of the interface, or a number of other factors influencing adhesion. We have used evaporation rates of 2.5 and 10 Å/s. Changing this rate may result in more substantial adhesive interactions.

Since, during adhesive failure, the bulk of the gold was removed while the monolayer was left apparently intact, failure occurred at or near the monolayer-gold interface. For the methyl-terminated monolayer, the failure within the composite was probably sharply localized at the hydrocarbon-gold interface. When the monolayer contained sulfur, however, gold remained on the surface in quantities approximately equal to sulfur (Au/S = 0.9–1.0). This observation suggests that the zone of failure was located within the gold itself, possibly between the first and second monolayers of gold at the monolayer-gold interface. Such a failure mode is possible if the gold-sulfur interface actually consisted of a monolayer of Au(I) coordinated to the sulfur. The formation of this type of interface is represented by Eq. (1). This supposition is

$$RSH + Au(0)_n \xrightarrow{[O]} RS^{-}Au(I)/Au(0)_{n-1} \qquad (1)$$

consistent with the observation that the gold remaining on the sulfur-terminated monolayer was oxidized relative to Au(0).

We have not been able to establish whether the gold remaining on these monolayers after adhesive failure was organized in microscopic islands. The amount of residual gold on the silicon substrates was too small to permit the use of scanning Auger to map its distribution. In the XPS spectrum, however, the observation of a single, oxidized gold environment suggests that the gold on the surface after adhesive failure was present as a monolayer. If the gold had been present in relatively thick (> 100 Å) islands, the binding energy of the gold would have been that of bulk Au(0) and any oxidized layer would, because of its low intensity, have been unobservable.

Gold adhered to both the thiol- and thioacetate-terminated monolayers. The XPS spectra suggest that, despite the differences in the constitution of the initial monolayers, the chemical composition of the monolayer-gold interface after deposition of the gold film was the same for these two systems. The sulfur and gold in these two systems exhibited experimentally indistinguishable binding energies and the acetyl (—$COCH_3$) group had disappeared from the thioacetate. While the chemical processes that result in loss of acetyl during reaction of gold with the thioacetate are unknown, it appears that the mechanism of adhesion for gold on the thiol- and thioacetate-terminated monolayers involved the same chemical bond.

IV. EXPERIMENTAL SECTION

A. General

Chemicals: 11-bromoundecene (Pfaltz and Bauer), thiolacetic acid (Aldrich), dihydrogenhexachloroplatinate(II) (Alfa), and trichlorosilane (Petrarch) were used as-received. Methylene chloride was distilled from CaH_2. Chloroform (Mallinckrodt), absolute ethanol (USI), diethyl ether (Mallinckrodt), and hexanes (Fisher) were used as-received.

B. 10-undecenyl thioacetate

Sodium (2.2 g, 97 mg-atom) was dissolved in absolute ethanol (200 mL) in a 500-mL round-bottomed flask equipped with a sidearm. The flask was sealed with a septum and the solution was purged of dioxygen by bubbling argon gas through it. Thiolacetic acid (7.8 mL, 109 mmol) was added with a gas-tight syringe. The solution was stirred for 30 min, after which 11-bromoundecene (13.0 g, 60 mmol) was added. The solution was heated at reflux (135 min) and stirred for a further 15 h. The solvent was evaporated and the remaining oil was dissolved in 200 mL of hexane. This solution was extracted with water (2 × 200 mL). The aqueous extracts were combined and extracted with hexane (100 mL) which was added to the original organic solution. The solvent was evaporated and the resulting oil was eluted with 93:7 (v/v) hexanes/ether through a silica column (230–400 mesh, diameter–4 cm, length–50 cm). The fractions that contained the product were combined and the solvent was evaporated. The remaining oil was distilled in a Kugelrohr apparatus. A fraction was collected that boiled between 53 °C (0.003 Torr) and 74 °C (0.008 Torr). The product (11.6 g, 51 mmol, 85%) was isolated as a yellow oil. ^1H NMR ($CDCl_3$): δ 5.8 (m, 1), 4.9 (m, 2), 2.8 (t, 2), 2.3 (s, 3), 2.0 (m, 2), 1.5 (m, 2), 1.4–1.2 (m, 14). Anal. Calcd. for $C_{13}H_{24}OS$: C, 68.35; H, 10.61; S, 14.03. Found: C, 68.30; H, 10.75; S, 14.12.

C. 11-trichlorosilylundecyl thioacetate (1)

This compound was prepared by hydrosilylation[34] of 10-undecenyl thioacetate. Trichlorosilane (3.6 mL, 36 mmol), 10-undecenyl thioacetate (5.0 g, 22 mmol), and dihydrogenhexachloroplatinate(II) (2.5 mL of a 0.01 M solution in THF, 0.025 mmol) were placed under argon in a dry heavy-walled glass tube (diameter–2.5 cm, length–21 cm) equipped with a sidearm, a 0–10 mm Teflon® stopcock, and a stirring bar. The solution was degassed (freeze-pump-thaw, 3 cycles) and the tube was sealed under vacuum at −195 °C. The tube was then warmed to room temperature and heated in an oil bath (98 °C, 41 h). After the tube had been cooled to −195 °C, a liquid nitrogen-cooled condenser was attached. The product was then warmed to room temperature and the excess trichlorosilane removed by a trap-to-trap distillation. The remaining liquid was transferred to a dry Kugelrohr distillation apparatus and a fraction was collected that boiled between 70 °C (0.004 Torr) and 112 °C (0.005 Torr). This crude material (7.09 g) was then distilled in a dry short-path still and the fraction that boiled between 112 °C (0.026 Torr) and 122 °C (0.024 Torr) was collected. The product (4.48 g, 12 mmol, 56%) was isolated as a clear oil. ^1H NMR ($CDCl_3$): δ 2.8 (t, 2), 2.3 (s, 3), 1.7–1.2 (m, 20). ^{13}C NMR ($CDCl_3$): δ 195.1, 31.69, 30.46, 29.43, 29.36, 29.31, 29.21, 29.06, 28.99, 28.89, 28.72, 24.28, 22.20. Anal. Calcd. for $C_{13}H_{25}Cl_3OSSi$: C, 42.91; H, 6.94; Cl, 29.23; S, 8.81. Found: C, 42.88; H, 6.89; Cl, 29.30; S, 8.90.

D. Preparation of monolayers

Silicon (100) substrates were standard boron-doped semiconductor grade silicon in 3 in. diameter wafers from Monsanto. The wafers were cut into 4 × 1.5-cm strips. These strips were cleaned by heating in a solution of conc. H_2SO_4 and 30% H_2O_2 (70:30 v/v) at 90 °C for 30 min.[18] *(Caution: 'piranha solution' reacts violently with many organic materials and should be handled with great care.)* The substrates were rinsed with doubly-distilled water and stored under water until use.

Solutions of **1** in methylene chloride (~ 1 mM) were prepared in a dry, nitrogen atmosphere. The substrates were placed in solution for 24 h and then rinsed in CH_2Cl_2. After this wash the substrates were removed from the dry atmosphere and rinsed in $CHCl_3$ and ethanol to remove any organic contaminants. The sample was then rinsed with ethanol dispensed from a pipette. The monolayer was dried under a stream of argon and contact angle and ellipsometry measurements were made immediately.

E. Hydrolysis

The substrates with the thioacetate-terminated monolayers were hydrolyzed in conc. HCl at 70 °C for 1.5 h. The wafers were removed from the acidic solution, rinsed with distilled water (2 × 20 mL) and ethanol (2 × 20 mL), and dried under a stream of argon.

F. Characterization

Contact angles were measured on sessile drops using a Ramé-Hart Model 100 contact angle goniometer equipped with a controlled environment chamber. All measurements were made at >80% relative humidity on 3-μL drops. The reported values are an average of eight measurements and have a precision of ±3°. Ellipsometric data were determined with a Rudolph Research Model 43603-200E thin film ellipsometer equipped with a He-Ne laser (λ = 6328 Å). The angle of incidence was 70.0° and the compensator was set at −45°. Analyzer (A) and polarizer (P) angles in zones 1 and 3 were determined for both the silicon substrate and for the substrate coated with a monolayer film. Values for A and P were averages from four different locations on the sample separated by at least 1 cm. The individual angles had a maximum scatter of 0.15°. The four locations were, by visual inspection, approximately the same for the bare substrate and for the monolayer. The refractive index for each substrate was determined from A and P for that substrate. The thicknesses of the monolayers were estimated using the algorithm of McCracken,[35] assuming a refractive index of 1.45 for the monolayer. Although the thioacetate group probably has a refractive index different from the hydrocarbon in the monolayer, the error introduced into the estimation of the thickness by assuming a homogeneous monolayer is less than 1 Å.

XPS spectra were acquired with a Surface Science Laboratories Model SSX-100 spectrometer with a monochromatized Al K_α x-ray source (10^{-8}–10^{-9} Torr). Spectra were referenced to Au $4f_{7/2}$ at 84.0 eV. For each sample a survey spectrum (resolution 1.1 eV, spot size 1000 μm, 1 scan) and high resolution spectra (resolution 0.16 eV, spot size 300 μm, 10–30 scans) of the C 1*s*, O 1*s*, Si 2*p*, S 2*s*, and Au 4*f* regions were taken. Atomic compositions were determined using standard multiplex fitting routines with the following sensitivity factors: C 1*s*, 1.00; Si 2*p*, 0.90; O 1*s*, 2.49; S 2*s*, 1.48; Au 4*f*, 19.08.[36] Binding energies were referenced to an average of the C 1*s*, Si 2*p*, and O 1*s* signals. Changes in the binding energies due to shifts in the reference were less than 0.2 ± 0.1 eV.

Electron micrographs were obtained with a JEOL JSM-35 scanning electron microscope.

G. Gold evaporation

Gold layers were prepared by downward thermal evaporation. Evaporations were performed at 4 × 10^{-7} Torr at rates of 2.5 and 10 Å/s. The thickness of the gold was monitored using an oscillating quartz crystal.

H. Adhesion tests

Peel strengths were measured using an Instron model 1101 tester. Because the silicon substrates were fragile, they were glued to aluminum pieces before attachment to the instrument. Strips of consumer grade Scotch™-brand Magic tape (cat. no. 105) were applied to the surface and, using a cotton swab, pressed into intimate contact with the gold. Adhesive strengths were measured for a 180° peel test at rates of 1 and 100 mm/min.

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[21] The thioacetate was subjected to acidic rather than basic hydrolysis since monolayers from alkyltrichlorosilanes are not stable in base.

[22] This range is not significant. Ellipsometric measurements for organic monolayers on silicon have a precision of $\pm$ 2 Å.

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[27] We do not know whether this binding energy indicates the presence of a thiol or of a disulfide. The difference in the binding energies of the S $2p$ electrons in a thiol (163.3 eV) and a disulfide (163.0 eV) is small. Values for the S $2s$ electrons are expected to differ by similar amounts. The difference in these binding energies is similar to the errors in our reference peaks. See Refs. 13 and 26.

[28] Adhesive failure for the thiol-terminated monolayers occurred, on average, in ~15% of the total area covered by the tape. On individual samples failure was found over 2–50% of the surface. For the thioacetate-terminated monolayers, failure occurred only on 25% of the samples and removed gold from less than 1% of the area covered by the tape. We believe that this difference in failure rates probably reflects contamination of the thiol interface during the hydrolysis of the thioacetate group.

[29] Since the monolayers prepared from HTS were longer than those created from **1**, the Au/C ratio exaggerates the difference in the amount of gold left on these surfaces. Comparisons to the Si $2p$ signal, which underestimates this difference, indicate that at least six times as much gold was left on the thiol-terminated interface as on the methyl-terminated one.

[30] The binding energy of the gold is referenced to an average of the C $1s$, O $1s$, and Si $2p$ signals.

[31] The binding energy of the sulfur in the thiol-terminated monolayer (228.4 eV) was between that of the sulfur in the thioacetate group (228.7 eV) and that of the sulfur in the thiol bound to the gold (228.0 eV). Uncertainties in the reference peaks were, however, almost as large as this shift.

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