

Tribology of Monolayer Films: Comparison between *n*-Alkanethiols on Gold and *n*-Alkyl Trichlorosilanes on Silicon

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This Article presents a quantitative comparison of the frictional performance for monolayers derived from *n*-alkanethiols on gold and *n*-alkyl trichlorosilanes on silicon. Monolayers were characterized by pin-on-disk tribometry, contact angle analysis, ellipsometry, and electrochemical impedance spectroscopy (EIS). Pin-on-disk microtribometry provided frictional analysis at applied normal loads from 10 to 1000 mN at a speed of 0.1 mm/s. At low loads (10 mN), methyl-terminated *n*-alkanethiolate self-assembled monolayers (SAMs) exhibited a 3-fold improvement in coefficient of friction over SAMs with hydroxyl- or carboxylic-acid-terminated surfaces. For monolayers prepared from both *n*-alkanethiols on gold and *n*-alkyl trichlorosilanes on silicon, a critical chain length of at least eight carbons is required for beneficial tribological performance at an applied load of 9.8 mN. Evidence for disruption of chemisorbed alkanethiolate SAMs with chain lengths $n \leq 12$ is shown through EIS analysis of tribology wear tracks. The direct comparison between the tribological stability of alkanethiolate and silane monolayers shows that monolayers prepared from *n*-octadecyl dimethylchlorosilane and *n*-octadecyl trichlorosilane withstood normal loads at least 30 times larger than those that damaged octadecanethiolate SAMs. Collectively, our results show that the tribological properties of monolayer films are dependent on their internal stabilities, which are influenced by cohesive chain interactions (van der Waals) and the adsorbate–substrate bond.

Introduction

Self-assembled monolayers (SAMs) are molecular films that can provide dense, two-dimensional sheets of surface functionality to impact interfacial properties.¹ SAMs have been used in a wide range of applications, such as the mitigation of protein adsorption,² promotion of selective attachments,^{3,4} generation of surfaces with varying wettability,⁵ and lubrication between contacting surfaces.^{6–9} In the latter regard, the lubricating properties of a variety of different monolayer films on silicon^{9–11} and gold^{12–15} surfaces have been investigated in an effort to reduce friction and prevent wear during operation. The ability to tailor the properties of SAMs by manipulating the composition of the

precursor molecule yields a versatile class of materials with which to investigate molecularly thin lubrication schemes, particularly in microelectromechanical systems (MEMS) where surfaces are separated by as few as 1–2 nm.¹⁶ At these small scales, the surface to volume ratio for a typical component is very high, and as a result surface forces dominate and adhesion, stiction, friction, and wear become significant technological barriers to the successful application of durable devices. The ability to functionalize the terminus of the SAM and vary the length of the assembling molecules provides a wide range of possible films and surfaces, each with differing tribological properties and interfacial interactions.

Monolayer films offer distinct advantages over many classical strategies for lubrication⁷ of MEMS devices because the molecular components can assemble onto all surfaces, even within nanoscale crevices between moving components, or onto targeted surfaces by matching the adsorbate headgroup with the metal or oxide surface. Silane-based films are generally preferred in tribological applications¹⁷ over thiolates because of the stronger covalent attachment of silanes compared to the weaker chemisorption of thiols on gold, silver, or copper. In addition, most MEMS devices are fabricated from silicon,¹⁶ and therefore, interest in lubrication of silicon-based devices has led to several studies on the tribological properties of silane monolayers,^{6,8,17–19} which are often prepared by the reaction of *n*-alkyltrichlorosilanes with surface silanol groups. Nonetheless, alkanethiolate SAMs on gold are also of keen interest in tribological studies due to their

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widespread use in the modification of many surfaces^{1,20} and the requisite, yet varied, mechanical requirements for these films.^{21–23}

With the recent growth in MEMS development, the measurement of the frictional properties of monolayers has become increasingly important. Several techniques are available to probe the interactions between surfaces including atomic force microscopy (AFM),^{11,13,15,17,24–26} surface force apparatus (SFA),^{27,28} and pin-on-disk tribometry.^{17,19,29,30} AFM and friction force microscopy (FFM) have been widely used for tribological studies and can provide information on the roughness,^{27,31} friction,^{8,23,28} wear,³² and lubrication¹⁰ of films. AFM experiments are conducted at sliding speeds ($\sim 1 \mu\text{m/s}$) that are several orders of magnitude lower than application speeds for MEMS devices (0.1 to over 500 m/s³³), resulting in frictional properties that may not be in the correct regime for practical applications. AFM-based studies also lack the ability to investigate normal loads greater than $\sim 100 \text{ nN}$; although, the contact pressures applied in AFM are on the order of $\sim 10^9 \text{ Pa}$.²⁸ Macro- and microscale friction and wear tests also have been reported in the literature using a pin-on-disk tribometer.^{17,19,29,30} A microtribometer enables the study of a broad range of sliding speeds (10 $\mu\text{m/s}$ to 10 mm/s), normal loads, and tip composition; the ability to vary both the tip and the normal load, as in the current work, allows for measurements at higher forces while maintaining low to moderate surface pressures ($< 300 \text{ MPa}$).

Molecular films have shown promise for the lubrication of surfaces, including both alkanethiolate SAMs on coinage metals^{15,23,24,30,34,35} and silane monolayers on silicon.^{6,8,9,17,18} Individual studies have focused on the effects of chain length, packing, and functionality of contacts. Specifically, Lio et al.¹² and McDermott et al.¹³ demonstrated that alkanethiolate monolayers formed from longer precursor molecules are more ordered and possess denser packing than shorter molecules. Their results suggest that the higher order and degree of packing for SAMs with longer chains are correlated with a reduced coefficient of friction. In addition to monolayer thickness, the functionality of the monolayer terminus has been shown to play an important role in frictional properties.^{19,36,37} Clear and Nealey⁸ showed that adhesion and friction were dependent upon monolayer terminus and solvent when performing chemical force microscopy with

thiol-coated gold tips and trichlorosilane-coated silicon substrates. The frictional force is larger for polar termini than for nonpolar termini for all solvents studied. Evidence of probe tip influence has also been reported where similar functionalities between two contacting surfaces display greater adhesion and therefore a higher coefficient of friction than when the two have dissimilar termini.^{8,15,38} Although studies of the frictional properties of monolayers by AFM and pin-on-disk tribometry are performed at vastly different forces and contacting areas, results from both types of testing have been shown to be consistent.¹⁷

Here, we report frictional properties for monolayers prepared from both ω -terminated alkyl thiols on gold and *n*-alkyltrichlorosilanes on silicon surfaces by using microtribometry. Through our experiments, we compare the tribological performance of alkanethiolate SAMs while varying chain length and terminal group functionality. We also provide a quantitative comparison of the performance of monolayers derived from *n*-alkanethiols on gold and *n*-alkyltrichlorosilanes on silicon that were subject to identical conditions. To our knowledge, the only reported comparison of *n*-alkanethiolate and silane monolayers was based on monofunctional hydrocarbon silanes that do not cross-link at the silicon (oxide) surface.¹⁷ Here, we focus on the more widely studied silane monolayers on silicon (oxide) prepared from *n*-alkyltrichlorosilanes, which can cross-link into robust coatings, along with alkanethiolate SAMs on gold. Therefore, a direct comparison between these two monolayer systems can be made, and their differences, which have been generally accepted but rarely quantified, may be better understood. Our results demonstrate that the tribological properties of monolayer films are dependent on their surface group as well as their internal stability, which depends on chain length and substrate–adsorbate bonding.

Experimental Section

Materials. Water used in all experiments was deionized (DI) and purified to $16.7 \text{ M}\Omega \cdot \text{cm}$ with a Modu-Pure system. Ethanol (absolute) was used as received from AAPER. All reagents were used as received. 1-Butanethiol, 1-hexanethiol, 1-heptanethiol, 1-octanethiol, 1-decanethiol, 1-dodecanethiol, 1-hexadecanethiol, 1-octadecanethiol, 11-mercapto-1-undecanol, and 11-mercapto-1-undecanoic acid were purchased from Aldrich. *n*-Octyltrichlorosilane, *n*-octadecyltrichlorosilane, and *n*-octadecyl dimethylchlorosilane were purchased from United Chemical Technologies (UCT). 1-Docosanethiol was purchased from Narchem Inc. Butyltrichlorosilane, hexyltrichlorosilane, dodecyltrichlorosilane, and hexadecyltrichlorosilane were purchased from Gelest. Fifteen centimeter polished, p-doped silicon wafers (100) were purchased from Montco Silicon. The silicon wafers were rinsed with ethanol and water and then dried in a stream of nitrogen prior to use. Gold shot (99.99%) and chromium-coated tungsten filaments were obtained from J&J Materials and R. D. Mathis, respectively. Nitrogen gas was purchased from A-L Compressed Gases.

Monolayer Preparation. *Gold.* Gold surfaces were prepared by evaporating gold shot onto silicon wafers. A chromium adhesion layer (100 Å) was deposited before gold (1250 Å) was evaporated onto the silicon wafers. Depositions were performed sequentially in a diffusion-pumped chamber with a pressure $< 5 \times 10^{-6} \text{ Torr}$ at a rate $< 2 \text{ Å s}^{-1}$. Wafers were stored at ambient conditions and typically cut into $1.5 \times 4.5 \text{ cm}^2$ samples. All samples were rinsed with copious amounts of absolute ethanol and dried in a stream of nitrogen before modification or testing. Gold substrates were immersed in a 1 mM solution of the

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alkanethiol in ethanol for 24 h. The resulting films were rinsed with copious amounts of absolute ethanol and dried in a stream of nitrogen before analysis and testing

Silicon. Silicon wafers were cut into $1.5 \times 4.5 \text{ cm}^2$ samples for surface modification and subsequent testing. Silicon substrates were sequentially sonicated in soapy water or ethanol for 30 min, treated with piranha solution (70% H_2SO_4 /30% H_2O_2) for 30 min, rinsed with copious amounts of water, dried with a nitrogen stream, and then immersed in a 1 mM solution of an alkyl trichlorosilane in toluene for 5 h. Samples were rinsed with toluene and dried in a stream of nitrogen.

Contact Angle Measurements. Contact angles of water and hexadecane were measured with a Rame-Hart manual contact angle goniometer. Advancing and receding contact angles were obtained on both sides of $\sim 10 \mu\text{L}$ drops with the syringe in the probe droplet during measurements. Reported values and errors reflect the average and standard deviation of measurements on at least five independently prepared films.

Ellipsometry. Ellipsometric thicknesses were determined from a J. A. Woollam XLS-100 variable-angle spectroscopic ellipsometer. Thicknesses were fit to data taken at 75° from the surface normal over wavelengths from 200 to 1000 nm. The sample surface was modeled as a 0.5 mm Si substrate with an oxide layer and a Cauchy layer. The thickness of the oxide layer was measured from a piranha-treated silicon substrate each time samples were prepared. The thickness of the monolayer film was calculated with an index of refraction set to 1.46 (the second Cauchy coefficient was set to zero), using the software's "normal fit" application.

Microtribometry. A Center for Tribology (CETR) UMT-2 Micro-Tribometer was used for all tribology experiments. The instrument was used for ball on flat surface sliding experiments with a 2-D FVL or 2-D DFM-0.5 force sensor, depending on the load to be applied. The FVL sensor is capable of measuring forces from 1 to 100 mN in both dimensions with a resolution of 0.01 mN for an applied load between 5 and 30 mN, while the DFM-0.5 sensor can apply loads ranging from 50 to 5000 mN and measure with a resolution of 0.25 mN. Tests were performed with a stainless steel ball bearing as the probe tip attached to the sensor via a suspension-mounting cantilever where the size of the tip was selected according to the magnitude of the applied load. The tip was sonicated in acetone for 5 min and dried with nitrogen before use. The FVL and DFM-0.5 sensors were operated with balls of 1 mm and 4 mm diameters, respectively. The force that the tip applied to the surface was slowly ramped to the desired load and allowed to equilibrate at that load for at least 15 s before the surface was set into motion. Tests were performed at a sliding speed of 0.1 mm/s over a 20 mm track for both unidirectional and multiple cycle wear tests. Results represent measurements on an average of five samples, each prepared independently. To estimate the contact pressure of the probe tip on the surface, the Hertz equation^{39,40} for deformation of a flat surface by a sphere was used,

$$P = \frac{1}{\pi} \left(\frac{4E_c}{3R} \right)^{2/3} F^{1/3} \quad (1)$$

where E_c is the composite Young's modulus, F is the normal load, and R is the tip radius. Using known values of elastic properties for gold ($E_{\text{Au}} = 77 \text{ GPa}^{41}$) and silicon substrates ($E_{\text{SiO}_2} = 70 \text{ GPa}^{42}$), a surface pressure for a normal load of 9.8 mN was calculated to be $\sim 250 \text{ MPa}$. Since the effect of a monolayer on the

Table 1. Water ($\theta_{\text{H}_2\text{O}}$) and Hexadecane (θ_{HD}) Contact Angles (Advancing, Receding) for Monolayers Prepared from *n*-Alkanethiols on Au and Both Octadecyl Dimethylchlorosilane and *n*-Alkyl Trichlorosilanes on Silicon Oxide

adsorbate/substrate	$\theta_{\text{H}_2\text{O}}$ ($^\circ$) ^a	θ_{HD} ($^\circ$) ^b
C ₂₂ SH/Au	110, 103	48, 40
C ₁₈ SH/Au	112, 102	48, 40
C ₁₆ SH/Au	106, 100	46, 37
C ₁₂ SH/Au	109, 96	45, 32
C ₈ SH/Au	106, 98	44, 30
C ₆ SH/Au	100, 94	28, < 15
C ₄ SH/Au	98, 85	< 15
HOC ₁₁ SH/Au	28, 19	< 15
HO ₂ C ₁₁ SH	38, 24	< 15
C ₁₈ SiCl ₃ /SiO ₂	110, 103	44, 40
C ₁₂ SiCl ₃ /SiO ₂	110, 103	40, 35
C ₈ SiCl ₃ /SiO ₂	109, 100	36, 28
C ₁₈ Si(CH ₃) ₂ Cl/SiO ₂	96, 80	32, 16

^a Standard deviation ± 4 . ^b Standard deviation ± 2 .

elastic properties of a substrate has not been established, this estimate does not account for monolayer films that would likely reduce our estimate of surface pressure. Due to the uncertainty of surface pressure, we report applied loads as forces in units of mN.

Electrochemical Impedance Spectroscopy (EIS). Electrochemical impedance spectra were obtained with a Gamry Instruments CMS300 impedance unit. A flat cell (EG&G) was used to expose 1.0 cm^2 of each sample selectively as the working electrode to an aqueous solution of 1 mM $\text{K}_3\text{Fe}(\text{CN})_6$, 1 mM $\text{K}_4\text{Fe}(\text{CN})_6$, and 0.1 M NaSO_4 . Measurements were obtained using a Ag/AgCl/saturated KCl reference electrode with evaporated gold on silicon as the counter electrode. Data were collected between 10^{-1} and 10^4 Hz using a 5 mV AC perturbation and fit using a Randles equivalent circuit⁴³ to determine the resistance and capacitance values of the SAM. When samples were tested by EIS following a pin-on-disk tribology test, 1 cm^2 of exposed sample area was centered around the tribology test track to yield an exposed track of $\sim 1.2 \text{ cm}$ in length and $\sim 0.01 \text{ mm}$ in width. Reported changes in capacitance and resistance of tested samples, therefore, are caused by tribometrically induced changes in the monolayer along this track ($\sim 1 \text{ mm}^2$), although the entire 1 cm^2 is tested in an impedance measurement.

Results and Discussion

Alkanethiols on Gold. To investigate the effects of SAM thickness and surface composition on frictional properties, we prepared monolayers onto gold substrates from a homologous series of methyl-terminated alkanethiols (C_nSH where $n = 4, 6, 8, 12, 16, 18,$ and 22) to form hydrophobic surfaces with known incremental increases in thickness, as well as monolayers of higher surface energy prepared from 11-mercaptoundecanol (HOC₁₁SH) and 11-mercaptoundecanoic acid (HO₂C–C₁₀SH). Table 1 shows the advancing and receding water and hexadecane contact angles for each monolayer studied. For $n \geq 8$, the advancing contact angles for water and hexadecane are $\geq 106^\circ$ and $\geq 44^\circ$, respectively, and are indicative of surfaces that have a predominate $-\text{CH}_3$ composition. Alkanethiolate SAMs with shorter chains ($n < 8$) do not present such dense CH_3 surfaces upon assembly; these SAMs provide a thinner barrier and less effective screening of forces between the liquid and the underlying metal. In general, longer molecules assemble to provide more van der Waals interactions among chains and yield a more densely packed film with fewer defects.⁴⁴ The polar terminal monolayers

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studied (i.e., hydroxyl and carboxylic acid) are completely wet by hexadecane and have advancing water contact angles $< 40^\circ$ that are consistent with higher energy surfaces.

Polar groups that exhibit stronger interactions with liquids may also interact with solid surfaces to increase the coefficient of friction (COF), which is the ratio of friction force to normal load and can be used to describe the ability of the film to lubricate the surface. Figure 1 shows the relationship between terminus functionality and coefficient of friction as measured with a 9.8 mN load at 0.1 mm/s over a 20 mm linear track. The SAMs in this figure are all of similar chain length and, therefore, have similar thicknesses, thus enabling investigation of the effect of the surface group on frictional performance. All SAM-modified substrates show a reduction in the coefficient of friction when compared to bare gold, regardless of the terminal functionality. Of the functionalities studied, the methyl-terminated film exhibited the lowest frictional force for the applied normal load (9.8 mN) as shown in Figure 1, reflecting weak interactions between the probe and the low energy surface. Friction values for SAMs with hydroxyl and carboxylic acid termini are similar and are $\sim 3\times$ higher than those for the methyl-terminated films. The hydroxyl and carboxylic acid termini have the ability to form hydrogen bonds and possess strong dipole moments; these forces allow for greater interactions between the probe tip and the underlying surface.

In addition to forming denser monolayer films, the abilities of molecules to form more stable layers on the substrate⁴⁴ and provide effective barriers against ion penetration⁴⁵ have also been linked to the length of the adsorbing molecule. For example, an alkanethiol of at least 10–12 carbons is required for assembly into SAMs that provide highly blocking barrier properties.⁴⁵ We hypothesize that the thicker films may also offer better mechanical protection to the underlying substrate because the stronger interactions between molecules provide the film with greater resistance against applied loads. The ability of the film to withstand an applied load can be characterized by measuring the friction force that results from movement of the surface against a normal load. Figure 2 shows the relationship between chain length of the adsorbed alkanethiolate monolayer and the coefficient of friction during a single-pass sliding test and indicates that a critical chain length of approximately eight carbons is required to obtain low coefficients of friction at this load (9.8 mN) and sliding speed (0.1 mm/s). We observed no improvement in the coefficient of friction when the surface was treated with *n*-alkanethiols that were longer than this critical value. This result is consistent with other tribological studies that show friction and adhesion forces to be independent of chain length when chains are longer than eight carbons.¹² Above this critical value, additive van der Waals forces are sufficiently strong to stabilize the film and provide highly effective lubrication of the substrate.

The single-pass sliding test used to determine the initial coefficient of friction in Figure 2 does not provide information on any damage that the tip may inflict on the monolayer. To investigate the amount of monolayer deformation caused by tribological testing, we performed electrochemical impedance spectroscopy (EIS) on alkanethiol-treated gold surfaces as the working electrode in a 0.1 M Na₂SO₄ (aq) solution containing 1 mM K₃Fe(CN)₆ and 1 mM K₄Fe(CN)₆, both redox-active species that can transfer electrons with the gold electrode. A sinusoidal potential perturbation of 5 mV was applied over the range of 10 000 to 0.1 Hz while measuring the impedance at each frequency, and the initial results (before tribological testing) are

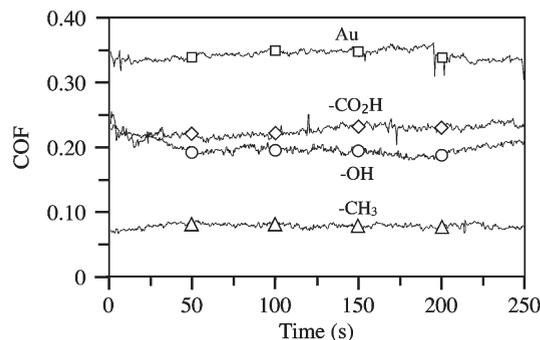


Figure 1. Effect of SAM terminal group on the coefficient of friction obtained with a 1 mm stainless steel ball at a sliding speed of 0.1 mm/s and a 9.8 mN applied load. SAMs were prepared from HO₂C(CH₂)₁₀SH, HO(CH₂)₁₁SH, and CH₃(CH₂)₁₁SH which all yield thicknesses of ~ 15 Å. The tribological test represents a single pass along a 2 cm line. The hydroxyl and carboxylic acid termini are both able to form hydrogen bonds and possess a strong dipole moment, which allows for greater interactions between the surface and the probe tip when compared to the methyl-terminated surface.

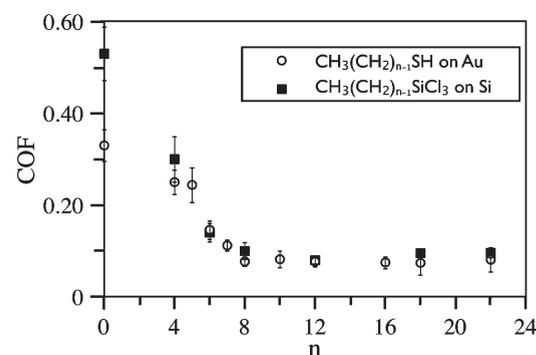


Figure 2. Effect of chain length (*n*) on the coefficient of friction for monolayers prepared from CH₃(CH₂)_{*n*-1}SH on gold and CH₃(CH₂)_{*n*-1}SiCl₃ on silicon. Tribology tests were performed at 0.1 mm/s for a load of 9.8 mN over a length of 2 cm. Error bars represent standard deviations where tests were repeated with at least five independent samples for each chain length studied.

shown as a Bode plot in Figure S1 in the Supporting Information. At high frequencies, the resistance due to ion transfer in solution can be measured due to the rapid alternation of potential that precludes the characterization of film properties. At intermediate frequencies, the SAM functions as a dielectric, characteristic of a straight line with a slope of -1 on the Bode plot, enabling measurement of the capacitive properties of the film. At low frequencies, the gradual change in potential allows sufficient time for ions to penetrate defects within the thinnest SAMs, resulting in a line of zero slope on the Bode plot and enabling the measurement of the resistance provided by the SAM against ion transfer. As shown in Figure S1 in the Supporting Information, the thinner films ($n = 6, 8$) exhibit spectra that contain a resistive plateau at low frequencies, signaling penetration of the redox probes into the SAM. The measured resistances of these thinner SAMs are 1.5–2 orders of magnitude lower than those for thicker SAMs ($n > 12$).

To determine any damage to the monolayer caused by the single tribometer pass, after initial characterization of the SAMs by EIS as described above, we subjected them to a single tribology test with a 9.8 mN load at a speed of 0.1 mm/s (during which contact pressures were approximately 250 MPa) for a length of 25 mm and then characterized the films by EIS again. The tribology

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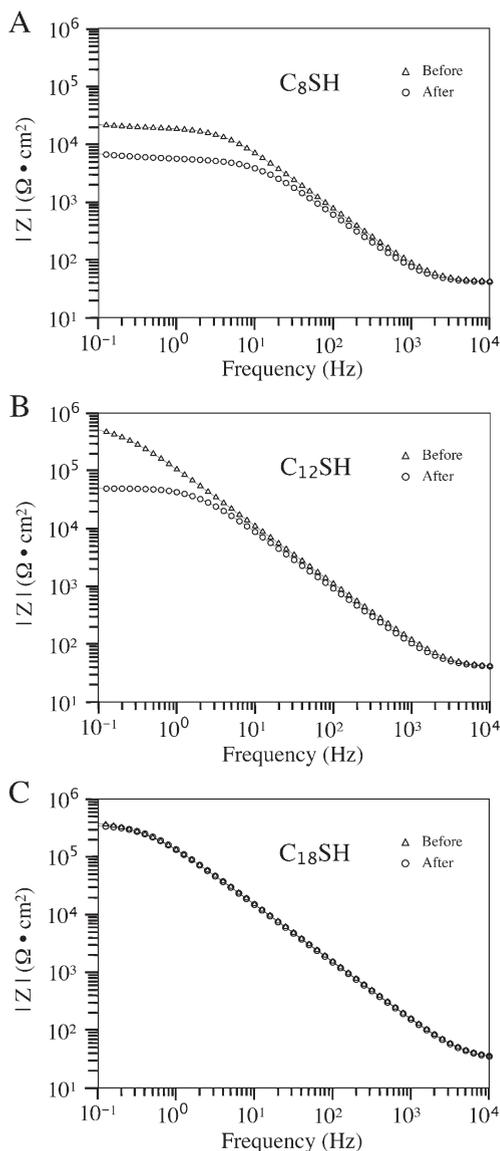


Figure 3. Effect of tribology testing on the impedance spectrum (Bode plot) of selected alkanethiolate SAMs on gold. SAMs were prepared from (A) C_8SH , (B) $C_{12}SH$, and (C) $C_{18}SH$. The impedance spectrum of each SAM was obtained before and after a 1 mm stainless steel ball was slid at a velocity of 0.1 mm/s at a force of 10 mN across the sample to produce a track of $\sim 10^{-2} \text{ cm}^2$, or 1% of the 1 cm^2 area tested by EIS. The electrolyte for impedance measurements consisted of 0.1 M Na_2SO_4 (aq), 1 mM $\text{K}_3\text{Fe}(\text{CN})_6$, and 1 mM $\text{K}_4\text{Fe}(\text{CN})_6$. Curves represent fits of the impedance data with a Randle's model equivalent circuit. Before tribometric testing, resistances were $2 \times 10^4 \Omega \cdot \text{cm}^2$ (C_8SH), $4 \times 10^5 \Omega \cdot \text{cm}^2$ ($C_{12}SH$), and $4 \times 10^5 \Omega \cdot \text{cm}^2$ ($C_{18}SH$), and after testing resistances were $6 \times 10^3 \Omega \cdot \text{cm}^2$ (C_8SH), $5 \times 10^4 \Omega \cdot \text{cm}^2$ ($C_{12}SH$), and $4 \times 10^5 \Omega \cdot \text{cm}^2$ ($C_{18}SH$).

test resulted in contact with the sample along a very small region of approximately 10^{-2} cm^2 of the 1 cm^2 of surface tested by EIS. This small area of contact is responsible for any changes in electrochemical performance of the film and demonstrates the disruption of a monolayer by such surface pressures. As a SAM becomes damaged, the redox species can diffuse through the defects within the SAM and donate/receive electrons from the gold electrode, which reduces the measured resistance against charge transfer. Further, the easier penetration of water and aqueous ions into the SAM would result in a marked increase in

Table 2. Capacitance Values Obtained before and after a Single Pass Tribology Test of 9.8 mN with a 1 mm Stainless Steel Probe Tip

molecule	capacitance ($\mu\text{F}/\text{cm}^2$)		ratio before/after
	before	after	
C_6SH	3.21	7.41	0.43
C_8SH	2.12	3.22	0.66
$C_{10}SH$	1.67	2.36	0.71
$C_{12}SH$	1.43	1.64	0.87
$C_{16}SH$	1.18	1.16	1.02
$C_{18}SH$	1.08	1.07	1.01
$C_{22}SH$	0.85	0.91	0.94

capacitance given the much higher dielectric constant of water (~ 78) versus that of alkyl chains (~ 2.1).⁴⁶ Figure 3 shows Bode plots before and after tribometric testing for SAMs on gold prepared from C_8SH , $C_{12}SH$, and $C_{18}SH$. Spectra for the two thinner SAMs (Figure 3A and B) show significant decrease in impedance at low frequency, which corresponds to a lower resistance or greater extent of defects within the SAMs after tip–SAM contact. The SAM prepared from $C_{18}SH$ (Figure 3C) is not affected by the tip–SAM sliding, as evidenced by impedance spectra that are nearly superimposable before and after tribometric testing. Although all three SAMs yielded indistinguishable coefficients of friction, only the thickest SAM has sufficient van der Waals interactions to maintain its integrity during the applied pressure.

By comparing the capacitance before and after the tribology test (Table 2), conclusions about the effects of applied load on the films can be drawn. If the capacitance before and after tribology testing is similar, the film has not been significantly altered by the contact with the probe tip; however, if the tip of the microtribometer has disrupted the film by removal of molecules or alteration of the chain packing density, the capacitance will increase as a result of a less effective charge separation and/or presence of ions within defects of the SAM. Although *n*-alkanethiols with chain lengths greater than 8 yield similar coefficients of friction, EIS studies show that the tip significantly damages SAMs with $n \leq 12$ as evidenced by the ratio of capacitance before and after the tribology test (Table 2). The results suggest that SAMs with $n = 16, 18$, and 22 have sufficient van der Waals forces to withstand the 9.8 mN applied load while SAMs derived from shorter alkanethiols do not contain sufficient internal stability to maintain the film structure during the single pass with the tribometer.

To further probe the tribological stability of the alkanethiolate SAMs on gold as a function of chain length (8–18), monolayers were subjected to various loads with the microtribometer (Figure 4). At the lowest load (9.8 mN), all monolayers displayed the capacity to withstand the applied force with a coefficient of friction of < 0.10 . As the load was increased, a thicker monolayer was required to maintain the frictional properties (i.e., a coefficient of friction of ≤ 0.10). However, for loads of 30 and 100 mN, no alkanethiolate monolayer tested was able to withstand the applied force. These results demonstrate that the greater cohesive interactions of the thicker SAMs cannot be disrupted unless a sufficient force is applied. For loads of 15 and 20 mN, only the $C_{16}S/Au$ and $C_{18}S/Au$ SAMs maintained their tribological performance observed at the lower load of 10 mN. These results show the effect of van der Waals interactions on film stability and indicate that the additivity of these relatively weak forces can stabilize monolayers, but only over modest increases in applied load.

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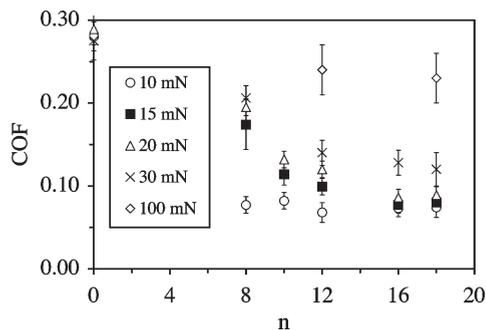


Figure 4. Effect of chain length (n) on the coefficient of friction for n -alkanethiolate SAMs on gold at different normal loads. Measurements reflect the average of a single-pass tribology test with a 1 mm diameter stainless steel probe tip at 0.1 mm/s for a length of 2 cm. Error bars represent standard deviations based on at least five independently prepared films.

Through use of AFM, Lio et al.³⁴ and Carpick and Salmeron⁴⁷ reported that when the force applied to the monolayer becomes large enough to overcome the cohesive interactions of the film, evidence of deformation of the SAM and underlying gold lattice was observed. At these loads, the probe tip has penetrated the SAM and has disrupted the interactions among chains, which can lead to the removal of molecules. If the load is increased above the point at which SAM disruption occurs, the tip was found to induce a transition in the lattice of the gold atoms from $(\sqrt{3} \times \sqrt{3})R30^\circ$ to (1×1) . The magnitude of this load or pressure is not well-known, but the phenomenon of disruption of the SAM is supported by our work. Liu and Xu⁴⁸ have designed a process referred to as “nanoshaving” where adsorbed alkanethiolate molecules are removed from the gold surface by applying a low load (0.3 nN) with an AFM tip in a solvent where molecules could reassemble on the surface when the nanoshaving technique is performed in an appropriate solution. These studies suggest that at low loads or contact pressures the deformation of the alkanethiolate monolayer on gold is reversible; however, at normal loads above a critical point or for scans over a prolonged time, the deformation extends into the gold substrate, thereby making the damage irreversible. The work presented here, where tribometric tests have been characterized by EIS, shows that for a load of 9.8 mN (~ 250 MPa) the probe tip imparts irreversible damage to monolayers with less than 16 carbon atoms. Our results show that the required load for destruction of the film depends on the cohesive energy of the SAM, and we hypothesize that the adsorbate–substrate interaction is also a key factor. A comparison between n -alkanethiolate SAMs on gold and silane monolayers is needed to test the hypothesis.

Silanes on Silicon (Oxide). A covalently bound monolayer film on hydroxylated silicon oxide surfaces was formed by exposure to a solution of n -alkyl trichlorosilane or n -alkyl dimethylchlorosilane in toluene. Trichlorosilane head groups condense to form silicon–oxygen bonds with surface silanol groups generated on the native oxide layer. Similarly, dimethylchlorosilanes offer the same covalent attachment to the substrate but without the ability to form additional siloxane bonds to the surface or other adsorbing molecules. Contact angles for silane monolayers are shown in Table 1 and are generally consistent with the formation of dense, methyl-terminated monolayer films derived from n -octadecyl trichlorosilane ($C_{18}SiCl_3$) molecules on

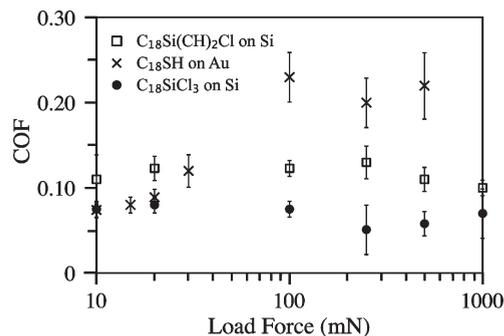


Figure 5. Effect of normal load, spanning 2 orders of magnitude, on the coefficient of friction for monolayers prepared from n -octadecanethiol on gold and both octadecyl dimethylchlorosilane and octadecyl trichlorosilane on silicon. Tribological performance was based on a single-pass tribology test at 0.1 mm/s on a track of 2 cm with stainless steel probe tips of 1 mm (for loads < 100 mN) and 4 mm (for loads ≥ 100 mN).

silicon oxide.^{8,17} As the chain length decreases, the n -alkyl trichlorosilanes form monolayers with surfaces that are rich in $-CH_3$ groups, as supported by water contact angles of $\sim 110^\circ$, but with some $-CH_2$ groups exposed, as indicated by reduced hexadecane contact angles. The monolayer prepared from n -octadecyl dimethylchlorosilane ($C_{18}SiMe_2Cl$) does not exhibit a dense methyl surface as indicated by the lower contact angles observed and reported in Table 1, consistent with a lower chain density as reported by Clear and Nealey.⁴⁹

The combination of van der Waals interactions, any intermolecular cross-linking, and headgroup attachment to the surface accounts for the cohesive energy of the alkylsilane films. While silanes have a more robust covalent attachment than the chemisorption of alkanethiolate SAMs, the differences in these stabilities have not been quantified. We have examined the tribological properties of silane monolayers on silicon (oxide) to compare with alkanethiolate SAMs on gold (Figure 2). Methyl-terminated films derived from n -alkyl trichlorosilanes exhibit a chain length dependence on friction at 9.8 mN loads that is nearly identical to those for n -alkanethiolate SAMs on gold. Films formed from C_4SiCl_3 and C_6SiCl_3 molecules show a modest improvement in coefficient of friction as compared to the bare silicon oxide substrate. However, a plateau of 0.09 in the coefficient of friction was observed for molecules with 8 or more carbons, such that increasing the chain length provided no additional tribological benefit or any decrease in performance. Monolayers derived from $C_{18}SiMe_2Cl$ on silicon (oxide) yielded a coefficient of friction of 0.12, 30% higher than that from n -octadecyl trichlorosilane ($C_{18}SiCl_3$), which we attribute to the less dense packing in the former film.⁴⁹

To probe the difference in tribological stabilities of alkanethiolate SAMs on gold and silane monolayers on silicon, we compared the coefficients of friction for monolayers prepared from $C_{18}SH$ on gold, as well as $C_{18}SiMe_2Cl$ and $C_{18}SiCl_3$ on silicon at a range of loads from 10 to 1000 mN (Figure 5). The only difference between these three molecules is the assembling headgroup; thiol molecules self-assemble on the gold substrate by chemisorption between sulfur and gold atoms, while silane monolayers are formed by a covalent siloxane bond between the silicon headgroup of the silane and the oxygen of the surface silanols atop the native oxide layer of the silicon substrate. Due to their identical carbon chain length, the films formed from these adsorbates

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should exhibit similar levels of van der Waals forces between the molecules, although the poor packing in the monolayer formed from $C_{18}SiMe_2Cl$ should result in the lowest cohesive energy of the three. While monolayers from alkanethiols and alkyl trichlorosilanes provided similar performances in initial tribological testing (Figure 2), the stronger covalent attachment of trichlorosilanes is demonstrated, as there is no change in the coefficient of friction for loads up to 1000 mN while the $C_{18}S$ -SAM begins to show a dramatic increase in friction at loads as low as 30 mN. Although the monolayer derived from $C_{18}Si(CH_3)_2Cl$ exhibits a higher initial coefficient of friction, this monolayer maintains its lubricity for all forces up to 1000 mN. Therefore, improved performance for silane monolayers over thiolate SAMs can be attributed to the strong covalent attachment of the silane molecule to the substrate and, for *n*-alkyl trichlorosilanes, the added ability of these adsorbates to intermolecularly cross-link between molecules,^{50,51} forming a robust siloxane network. Both features make removal or deformation of the monolayer more difficult than that for the alkanethiolate/Au system. The results presented here illustrate that silane films offer improved tribological properties over alkanethiolate SAMs on gold for high normal loads.

Collectively, our results show that the tribological properties of monolayer films are dependent on their internal stabilities, which are influenced by cohesive chain interactions (van der Waals) and the adsorbate–substrate bond. For a constant load, increases in chain length yield monolayers that are more stable against tribological deformation to provide low coefficients of friction. For a constant adsorbate chain length, a more stable bonding to the substrate correlates with the most stable lubricating monolayers. The fact that alkanethiolate SAMs on gold and silane monolayers on silicon exhibit similar chain length effects on friction at low loads (Figure 2), and vastly different performance at high loads (Figure 4), provides insight into the likely mechanism for tribological deformation of monolayer films. Stable

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interchain interactions can provide a buffer that prevents the probe from contacting the substrate at low loads. At higher loads, the probe disrupts these weak interchain interactions and can even dislocate adsorbates from their binding sites on the substrate. Thus, strong adsorbate–substrate bonds are required to maintain the integrity of the monolayer at these high loads.

Conclusions

Our results show that the tribological properties of monolayer films depend on the surface group, chain length, and headgroup of the adsorbate. At low loads (9.8 mN), methyl-terminated SAMs yield coefficients of friction that are 3-fold lower than those by hydroxyl- or carboxylic-acid-terminated SAMs of similar total chain length. Increasing the chain length of the adsorbate results in improved buffer properties of the monolayer to prevent probe–substrate interactions and the ability of the monolayer to withstand a higher normal load. Nonetheless, *n*-alkanethiolate SAMs with chain lengths $n \leq 12$ are irreparably damaged by a single pass of the probe at forces as low as 9.8 mN, whereas SAMs with longer chain lengths are more stable against the shearing forces of the probe. Monolayers prepared from *n*-octadecyltrichlorosilane and *n*-octadecyldimethylchlorosilane on silicon can withstand normal loads that are at least 30 times greater than those that disrupt $C_{18}S/Au$ SAMs on gold, owing to the stronger siloxane bonds of the silane monolayers. These results suggest that a tribological breakdown of cohesive, interchain interactions precedes displacement of molecular components for *n*-alkanethiolate SAMs on gold. Much stronger adsorbate–substrate interactions stabilize silane monolayers against tribological degradation.

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Supporting Information Available: Bode plots of alkanethiolate SAMs on gold. This material is available free of charge via the Internet at <http://pubs.acs.org>.