Tribological characterization of gradient monolayer films from trichlorosilanes on silicon

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HIGHLIGHTS

- ▶ We report the assembly of 1- and 2-component gradient monolayer films on silicon.
- ▶ Ellipsometry, contact angles, and tribometry verify gradient formation.
- ▶ 1-Component gradients exhibit a broad range of frictional coefficient.
- ▶ 2-Component gradients show good stability and a threefold change in friction.

GRAPHICAL ABSTRACT
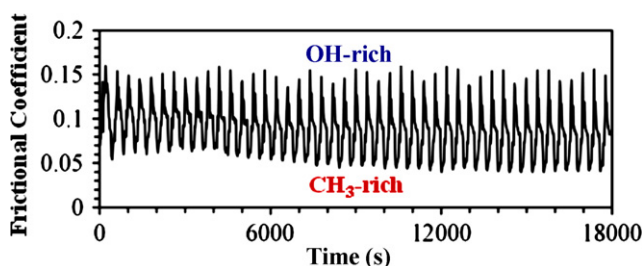
ABSTRACT

We report a simple and effective approach to assemble single- and dual-component gradient monolayer films of silane precursors onto a silicon substrate under ambient conditions. Characterization of these gradient films with water contact angles and ellipsometric thicknesses has been performed to confirm gradient formation with a high degree of repeatability. Tribological testing of these gradient films was also performed to determine the role that surface energy and dispersive forces within the monolayer have on the frictional performance of the resulting films. Our results show that the tribological properties of single-component gradient monolayer films prepared from octadecyl trichlorosilane on silicon are dependent upon the surface coverage and surface energy of the gradient monolayer. We also demonstrate that the coverage of a hydrocarbon monolayer is a critical aspect of the frictional response of the film by relating the tribological performance of gradient monolayers to that of pure monolayers with known thicknesses. Sparse monolayer regions are more prone to frictional failure by exposing more of the underlying substrate and further enabling the probe tip to impart the normal load to fewer adsorbed molecules to greatly increase the pressure per adsorbate. Two-component monolayers with methyl and hydroxyl termini offer much greater stabilities to prolonged cycling due to stronger intermolecular interactions that prevent probe–substrate interactions.

1. Introduction

The ability to control the surface energy of a substrate with a high degree of positional precision, such as creating gradients of surface energy [1], is an essential requirement for many applications, including directed droplet motion [2], biological detection and selective attachment [3–6], microfluidics [6], and chemical sensing [7]. Techniques that can produce consistent gradients of one or two component monolayers using alkanethiol [3,7] or n-alkyl trichlorosilane [6,8] precursors on gold or silicon surfaces, respectively, include diffusion through chromatographic media [7], ink jet printing [9], gradual immersion [4], laminar flow [5,10], controlled vaporization [2,11,12], controlled oxidation [13], contact printing [6,8], and photodegradation [14]. A potential disadvantage of forming gradient mixed monolayers with two or more different thiols is the tendency for phase separation of the identical chains

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and terminal groups to yield islands instead of a well-mixed gradient monolayer [4]. In contrast, exposure of a silicon surface to a mixture of n-alkyltrichlorosilanes generally yields well-mixed monolayers without macroscopic phase segregation [15,16] due to the formation of robust siloxane bonds on silicon and to adjacent adsorbates that minimize the role of weaker interchain interactions during assembly.

As silane-based monolayer films have begun to emerge as prime candidates for molecular lubricants in microelectromechanical systems (MEMS) components [17–21], the implementation of silane monolayer gradients to enable accelerating and decelerating contacts during operation is potentially attractive. Previously we have shown that low-energy monolayers prepared from n-alkyltrichlorosilanes yield low coefficients of friction if the chain length is >8, as this provides sufficient interchain cohesion to prevent probe–substrate interactions [22]. Furthermore, the tribological stability of these monolayers increases exponentially with increased chain length of the precursor molecules [23]. In addition, we have reported the tribological performance of two-component alkylsilane mixed monolayer films [16], indicating that with the proper pairing of components, these systems can provide frictional properties that are similar to the best single-component systems. While one and two component silane monolayer films have been studied for lubrication applications [16,20,22,24], gradient silane films have not been characterized in tribological testing. The ability to prepare precise, robust gradients is expected to be an important aspect in the future technological development and application of MEMS technologies.

Here we report the formation and characterization of gradient monolayer films based on one and two molecular components using a simple solution-based assembly method. We also report the tribological performance of these gradient monolayer films with a microtribometer using a 4 mm stainless steel ball bearing as the probe for tests conducted over the length of the gradient subjected to a load of 98 mN at a speed of 0.1 mm/s. Frictional tests were also performed cyclically to investigate the reproducibility of the lubricating performance.

2. Materials and methods

2.1. Materials

Water used in all experiments was deionized (DI) and purified to 16.7 MΩ cm with a Modu-Pure system. All reagents were used as received. Ethanol (absolute) and n-octadecyltrichlorosilane were purchased from AAPER and United Chemical Technologies (UCT), respectively. (1-Trichlorosilyl undecyl)trichloroacetate was available from a prior investigation [16]. 15 cm 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. Nitrogen gas was obtained from A-L Compressed Gases.

2.2. Monolayer preparation

2.2.1. Silicon substrate

Silicon wafers were cut into 1.5 cm × 4.5 cm samples, sonicated in ethanol for 30 min, rinsed with ethanol, and dried in a stream of nitrogen before being treated with piranha solution (70% H_2SO_4/30% H_2O_2) for 30 min, rinsed with copious amounts of water, and dried again in a stream of nitrogen. *Caution*: Piranha solution is a strong oxidizer and can be extremely dangerous. Piranha solution should never be stored and should be disposed of properly immediately after use.
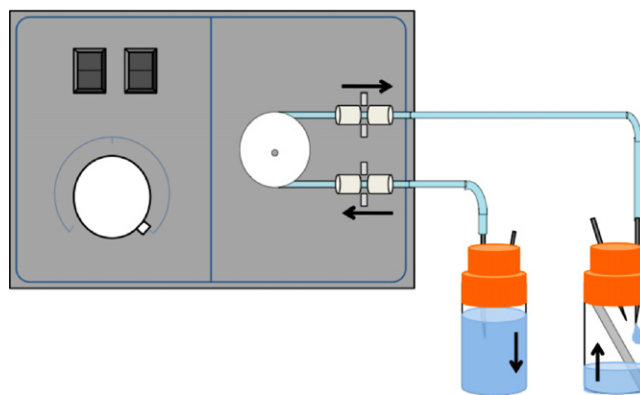

Fig. 1. Schematic illustration of the setup for silane gradient assembly where a peristaltic pump was used to add solvent at 1 mL/min to an initial 0.5 mL starting solution containing 0.5 mM $C_{18}SiCl_3$ and a silicon substrate.

2.2.2. Single-component octadecyltrichlorosilane gradient monolayers

Octadecyl trichlorosilane monolayers were formed by immersing the piranha-treated silicon samples into solutions of silane precursors in toluene at 23 °C and 35 ± 5% relative humidity. Assembly was performed in a 20 mL vial that initially contained 0.5 mL of 0.5 mM octadecyl trichlorosilane in toluene so that only the bottom of the substrate was immersed (∼0.3 cm). Toluene was added to the vial via a peristaltic pump at a rate of 1 mL/min for approximately 20 min using the setup as shown in Fig. 1. The concentration and time allowed for assembly varied with respect to position on the substrate in order to obtain a gradient of surface energy along the sample. Samples were removed from solution immediately upon the solution fully immersing the sample, rinsed in ∼20 mL of toluene, then rinsed with deionized water and ethanol, and dried in a stream of nitrogen. We have previously reported the characterization of densely packed monolayers prepared from octadecyl trichlorosilane, similar to ones used in this study, by contact angle analysis and ellipsometry [23].

2.2.3. Two-component gradient monolayers

Two-component gradient monolayers were prepared by immersing a single-component gradient monolayer, prepared as described above from n-octadecyltrichlorosilane, into a 1 mM solution of (1-trichlorosilyl undecyl) trichloroacetate in toluene at 23 °C and 35 ± 5% relative humidity for 1 h. The films were then removed from solution, immersed in 20 mL of toluene for 15 s, sequentially rinsed with ethanol, water, and again with ethanol, and then dried in a stream of nitrogen. The conversion of the trichloroacetate group into a hydroxyl was accomplished by immersion into a solution containing 10 mL of deionized water, 10 mL of methanol, and 0.15 g of sodium bicarbonate for 15 min. These films were then sequentially rinsed with ethanol, water, and ethanol, and then dried in a stream of nitrogen. The assembly of pure component hydroxyl monolayers by this route has been described by us previously [16].

2.3. Ellipsometry

Ellipsometric thicknesses were determined using a J.A. Woollam XLS-100 variable-angle spectroscopic ellipsometer. Three separate thickness measurements were taken across the width of the sample at 8 different locations along the length of the gradient, and the resulting average at each location was reported as the local thickness of the monolayer. Thicknesses were fit to data taken at 75° from the surface normal over wavelengths from 200 to 1000 nm. The sample was modeled as a 0.5 mm Si substrate with an oxide layer and a Cauchy layer [25]. The thickness of the oxide layer

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was approximated by measuring a piranha-treated silicon sample obtained fresh each time films were measured. The thickness for the hydrocarbon and OH-terminated monolayers were measured with an index of refraction set to 1.46 (the second Cauchy coefficient was set to zero for all monolayers). All monolayers were fit using the software's "normal fit" application. The reported values and errors reflect the averages and standard deviations of at least 3 independently prepared gradient films.

2.4. Contact angle measurements

Contact angles of water and hexadecane were measured with a Rame-Hart manual contact angle goniometer at 8 different locations along the gradient. Advancing and receding contact angles were obtained on both sides of approximately 10 μL drops with the syringe in the probe droplet during measurements. The reported values and errors reflect the average and standard deviation of at least 3 independently prepared gradient films.

2.5. Microtribology

A Center for Tribology (CETR) UMT-2 Micro-Tribometer was used for ball on flat surface sliding experiments with a 2-D DFM-0.5 force sensor. 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 4-mm stainless steel ball bearing as the probe tip attached to the sensor via a suspension-mounting cantilever. The tip was sonicated in acetone for 5 min and dried with nitrogen before use. The force that the tip applied to the surface was slowly increased 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 10 mm track for frictional coefficient measurements at a common relative distance and at a sliding speed of 0.1 mm/s over a track of 25 mm for probing of the gradient.

3. Results and discussion

3.1. Formation of single-component gradient monolayers

We have developed a versatile method with a simple design to fabricate one-component gradient monolayers formed from an octadecyl trichlorosilane precursor on silicon. Silicon substrates that were approximately 4.5 cm long and 1.5 cm wide were placed in a 20 mL glass vial containing ∼0.5 mL of 0.5 mM octadecyl trichlorosilane in toluene and capped with a rubber septum. The substrate was oriented nearly vertically so that only the bottom 0.5 cm of the substrate was initially immersed in solution. Toluene was subsequently added dropwise at a rate of ∼1 mL/min using a peristaltic pump as shown in Fig. 1 until the entire sample was completely submerged in solution (typically requires ∼20 min) and then immediately removed from solution and rinsed with toluene. Through this process of gradually increasing the level of precursor solution while simultaneously diluting the active trichlorosilane concentration, higher points on the vertically oriented sample were exposed to lower precursor concentrations for shorter periods of time, thereby controlling the number of molecules that are adsorbed to the substrate dynamically. Characterization of the films was performed using contact angle goniometry, ellipsometry, and microtribology. Water contact angles and ellipsometric thicknesses were taken at 5 mm increments across the sample to analyze the monolayer and confirm the formation of a gradient. Using a dimensionless distance scale, 0 is defined as the position on the surface that corresponds to the initial height of the precursor solution and 1 the position on the surface that corresponds to the final height of the precursor solution, which the sample is exposed to for only
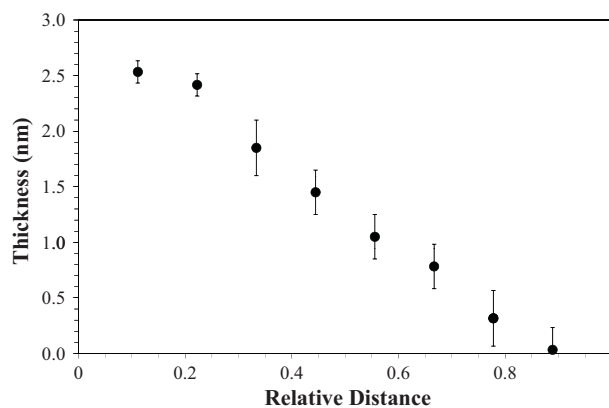

Fig. 2. The dependence of ellipsometric thickness on the relative distance along the substrate, demonstrating the formation of a gradient film. Here, the total gradient distance was 40 mm. A relative distance of 0 corresponds to the low-energy end of the sample (a dense C18 monolayer) whereas 1 corresponds to the high-energy end (a very sparse C18 monolayer).

a few seconds. Fig. 2 shows the measured thickness of the substrate at various points in the assembly process and demonstrates a thickness of 2.5 nm at a relative distance of ≤0.2 is consistent with a densely packed monolayer prepared from $C_{18}SiCl_3$. In the intermediate portion of the substrate (relative distance 0.2–0.8) the thickness decreases linearly until there is no measured thickness at high relative distances (≥0.8). In this intermediate region, the decrease in the number of adsorbed silane molecules results in a decrease in the measured thickness. At high relative distances where very small thicknesses were measured, some molecules have assembled on the substrate to form a sparse film in a conformation that maximizes interactions and minimizes free energy, i.e., by lying down to cover the substrate. There is potential for the octadecyl trichlorosilane precursor to assemble into islands on the substrate as reported for gradient alkanethiols on gold [3], but, as described below, island formation does not appear to be the dominant mode of arrangement in these submonolayer regions.

Fig. 3 shows the positional dependence of advancing water contact angles to demonstrate the hydrophobic and hydrophilic character of the extremes of the gradient with an intermediate wettability in the middle. The hydrophilic end (relative distance 1) of the substrate reaches a contact angle of 38° that is similar to the value for a bare silicon substrate exposed to pure toluene solvent for the same time as the experiments (37°), while the hydrophobic
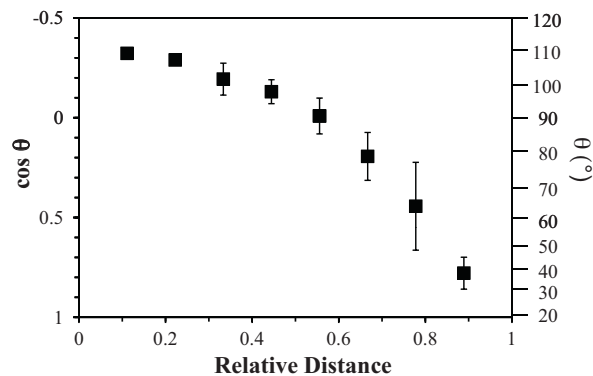

Fig. 3. The advancing water contact angle (right axis) and its cosine (left axis) measured at relative distances along the substrate for a single-component gradient monolayer prepared from $C_{18}SiCl_3$. Here, the total gradient distance is 45 mm. A relative distance of 0 corresponds to the low-energy end of the sample (a dense C18 monolayer) whereas 1 corresponds to the high-energy end (a very sparse C18 monolayer).

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end (relative distance 0) has a value of 110°, consistent with a well formed methyl-terminated monolayer [26].

Two methods have been used to determine the area coverage of the *n*-octadecyl chains in the gradient monolayers. First, the equation proposed by Cassie [27] was used to estimate the area coverage based on advancing water contact angles of the silane precursor on the substrate using contact angle measurements on methyl-terminated and control bare substrates:

$$\cos\ \theta = \sigma_{Cassie}\ \cos\ \theta_1 + (1 - \sigma_{Cassie})\cos\theta_2 \qquad (1)$$

where θ is the measured advancing water contact angle on the gradient monolayer, σ_{Cassie} is the area coverage of n-octadecyl chains on the surface, θ_1 is the advancing water contact angle of a pure monolayer prepared from octadecyl trichlorosilane (113°), and θ_2 the advancing water contact angle for a bare substrate that has been exposed to solvent (37°). Strictly, Eq. (1) provides the approximate coverage of methyl-terminated domains or islands on the surface. If the chains are not islanded but dispersed, they will cant further from the surface normal, exposing methyl and methylene groups to provide increased hydrophobic area, leading to higher measured coverages as compared to those for the same number of molecules on an islanded surface. Secondly, the ratio of measured ellipsometric thickness (*d*) to the thickness of a dense monolayer prepared from octadecyl trichlorosilane monolayer (d_{pure}) was used to estimate coverage [28]:

$$\sigma_{thickness} = \frac{d}{d_{pure}} \qquad (2)$$

where $\sigma_{thickness}$ is the area coverage as determined by thicknesses and d_{pure} is 2.5 nm. Fig. 4 shows the correlation between $\sigma_{thickness}$ and σ_{Cassie}. For the majority of the gradient film (relative distances of 0.3–0.9) the area coverage of bound octadecyl siloxane molecules as estimated by Eq. (1) is greater than that estimated by Eq. (2). The deviation between the two coverage calculations suggests that adsorbates at low to intermediate coverages adopt conformations where the chains are more canted, as opposed to extending normal from the substrate. The higher cant of the bound molecules results in molecules occupying more space on the substrate to provide a greater hydrophobic footprint than the coverage as determined by ellipsometric thickness would suggest. Thus, the area coverage as determined from wetting tends to overestimate the number of molecules on the surface since Eq. (1) describes the behavior of a surface with discrete, segmented areas (CH_3 versus bare), and does not fully describe a gradual transition (CH_3, CH_2, bare) between states. This discrepancy indicates the molecules do not extensively form islands on the substrate but assemble into a film with a
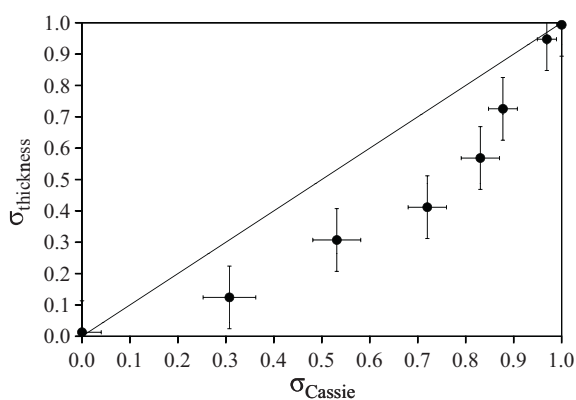
Fig. 4. Comparison of coverage as determined by thickness using Eq. (2) versus that determined by contact angles with Eq. (1). Deviation between the two techniques suggests that the molecules do not extensively assemble into islands on the substrate.
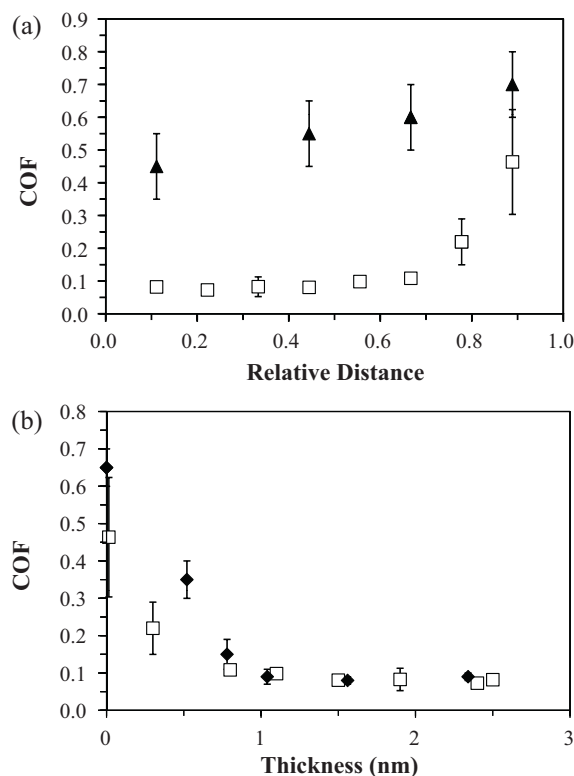
Fig. 5. (a) Dependence of the coefficient of friction (COF) on the relative distance (total distance = 25 mm) for single-component gradient monolayers prepared from $C_{18}SiCl_3$. Results for the gradient monolayer are shown as open squares and those for the control sample (not exposed to silane precursor; only toluene) are shown as triangles. Here, the sliding direction for each data point in the gradient monolayer is perpendicular to the gradient direction for (a) and (b). (b) Dependence of COF on thickness for a single-component gradient monolayer (open squares) as well as pure monolayers prepared from n-alkyl trichlorosilanes (*n* = 4, 6, 8, 12, 16, and 18) that are shown as solid diamonds. In both (a) and (b), the applied load is 98 mN and the probe velocity is 0.1 mm/s.

continuous gradient of surface energy. Our results are compatible with those of Flater et al. [29] who used atomic force microscopy to characterize the topography and friction of monolayers prepared by short exposure times (20 min) of silicon to octadecyltrichlorosilane. They observed both a densely packed phase and a disordered phase, with the disordered phase providing greater friction. At the lower-coverage sections of the gradients described here, Fig. 4 suggests that a disordered phase with significant chain canting is dominant.

The gradient monolayers prepared by our solution method demonstrate similar thicknesses and wetting behavior to previously reported silane gradient monolayers [2,6,8,30], while being simple to perform, repeatable, and easily tuned for samples of different dimensions. The loosely packed, sparse monolayer present at relative distances between 0.3 and 0.8 offers unique surface energies that have previously not been studied in tribological testing.

3.2. Tribology of single-component gradient monolayers

Fig. 5a presents the coefficient of friction for a one-component gradient monolayer prepared from octadecyl trichlorosilane on silicon at specific relative distances that correspond to differing surface energies. The CH_3-rich portions of the substrate (relative distance <0.3), as indicated by water contact angles and ellipsometric thicknesses (shown in Figs. 2 and 3) display a coefficient of friction (COF) of ~0.08 that is consistent with the COF of a densely packed monolayer prepared from octadecyl trichlorosilane.[23] When the conditions of assembly are manipulated to yield a film that is less

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dense and lacks the necessary dispersive forces to provide a stable barrier to the tribological load, the coefficient of friction increases due to greater probe–substrate interactions. The methyl-deficient end of the sample has a COF that is significantly higher than that of a well formed film but, due to the presence of a small number of chains on the surface, does not reach the value of a bare silicon substrate (0.6), as shown more clearly in Fig. 5b. This behavior reflects the observation that even a few adsorbed chains can measurably reduce the coefficient of friction. At relative distances >0.7 where the coverage of molecules is less than ~30%, the molecules must minimize their free energy by adopting a highly canted conformation to interact with other sparse molecules and even a completely horizontal conformation in some cases to interact with the substrate and thereby provide a thinner lubricating barrier. Fig. 5a also shows data for an uncoated silicon surface that was exposed to pure solvent (toluene) for the same amount of time as the coated films. These uncoated control samples exhibit values consistent with the known COF of silicon (0.6) except at low relative distances (<0.4). This result suggests that the high-energy bare substrate exposed to solvent is partially passivated by a very small number of physisorbed molecules resulting in a COF of 0.45 that is lower than the known value of 0.6 for a bare silicon substrate.

Fig. 5b shows how the frictional performance of the gradient film compares with that of well formed monolayers assembled from precursors of a fixed length. For a thicker gradient film corresponding to relative distances 0.1–0.7, the film behaves identically to a dense monolayer from $C_{18}SiCl_3$, even though the molecular coverage of the monolayer dips to ~30% at a relative distance of 0.7. While nanoscale tribology experiments have shown a slight difference in friction between dense and disordered C_{18} phases [29], these microscale experiments provide an area-averaged coefficient of friction that is insensitive to coverage of the C_{18} chains from 30% to 100%. As shown in our earlier work [23], a chain length of approximately 8 carbons (~1 nm) is required to provide a sufficiently cohesive monolayer that prevents probe–substrate interactions and achieve low coefficients of friction at this load and speed. The gradient monolayer behaves similarly, demonstrating the same plateau in COF at higher thicknesses that is observed for well-formed monolayers with lengths ≥8 carbons. When the thickness of the gradient film is reduced below 0.8 nm, the lubricating performance of the monolayer begins to decrease, as the film is not sufficiently robust to sustain the applied 98 mN tribological load. In the low thickness regime, the gradient monolayer does provide improved lubrication over the pure monolayer (prepared from C_4SiCl_3 and C_6SiCl_3), suggesting that long, liquid-like chains are more effective than a dense array of shorter chains having equivalent average thickness.

In order to determine the repeatability of the tribological performance of gradient films, frictional tests were run for several cycles (Fig. 6). These tribology tests focus on the performance of the portion of the gradient film (relative distance between 0.6 and 1.0) where we begin to see deviation from the tribological results for dense monolayers from octadecyl trichlorosilane that we have shown in previous work [23]. These tribology tests were performed to follow the surface energy of the gradient from low (relative distance of 0.6) to high (relative distance of 1.0) and then retrace the same path. The much steeper slope of the COF during the initial scan and at the beginning of the second scan demonstrates that the probe is altering the film. Similarly, the peak between the first scan and its retrace rises to a COF of 0.4 that is greater than at any other time during the wear test. We believe during the first scan the probe tip alters the film, perhaps aligning the sparse chains of the film. The frictional forces observed following this initial alteration exhibit more consistent behavior with a regular sawtooth pattern, reflecting the varied surface composition of the gradient. As the probe tip approaches the portion of the gradient that has a higher
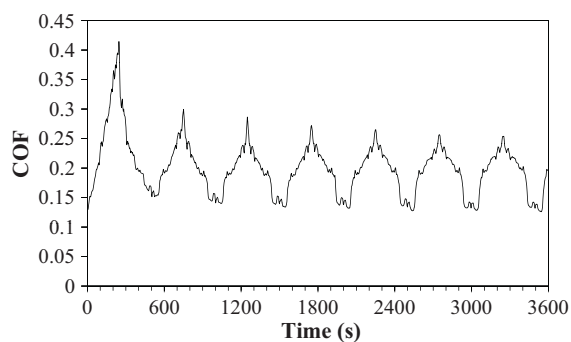

Fig. 6. Cyclic tribological scans focusing on the intermediate to sparse end of a single component gradient film (relative distance from 0.6 to 1.0) prepared from $C_{18}SiCl_3$. Each cycle lasted 500 s with a 98 mN load and a speed of 0.1 mm/s.

surface energy due to fewer adsorbed molecules, the COF steadily increases to a value of 0.3. At this sparsely populated end of the sample, the monolayer exhibits poor lubricating performance as the barrier between the probe and substrate is diminished. The broadening of the shoulder on each cycle is indicative of the rearrangement, and possible removal, of a small fraction of molecules from the substrate by the probe. The likely mechanism for tribological failure of silane monolayer films is the removal of individual molecules from the substrate as we have previously reported [23].

3.3. Two-component monolayer gradients

While single-component monolayer gradients exhibit a large range in the frictional coefficient, their long-term stability against tribometric sliding may be compromised due to the sparseness of the bound hydrophobic chains on the high-energy portion of the gradient. To address this issue of robustness, we have assembled a second component into the single-component gradients to create a two-component monolayer gradient. Here, we chose (1-trichlorosilyl undecyl)trichloroacetate as the second component because the trichloroacetate terminal group can be cleaved post-assembly to produce a hydrophilic hydroxyl terminus that would yield higher COFs than a methyl-terminated monolayer [16]. However, due to the bulkiness of the original trichloroacetate terminus, the resulting hydroxyls have larger intermolecular spacing than in a dense hydroxyl monolayer and so the underlying methylene groups are also exposed at the surface. Thus, the final surface energy is reduced below that of a dense hydroxyl-terminated monolayer or an uncoated silicon surface [16]. Fig. 7a shows the advancing water contact angle with relative distance along the two-component gradient, illustrating a general trend of increased wettability with increasing distance as additional free space exists for the deposition of the hydrophilic component. The range of contact angles observed is from 114° at the low-energy end to 68° at the high-energy end, where the latter value is increased above that for a mostly uncoated silicon surface (~38°), as shown in the single-component gradient of Fig. 3. The value of 68° is close to that of 64° that has been reported for pure hydroxyl monolayers prepared by this two-step assembly route [16]. Fig. 7b shows how the COF is affected by repeated tribometric scanning across the two-component gradient, exhibiting a range of 0.04–0.06 on the low-energy end and a value as high as ~0.16 on the high-energy, hydroxyl-rich end. The gradient is stable, as evidenced by a relatively constant frictional performance over the entire 18,000 s (5 h) run. This boost in stability and the more constant performance in comparison to a single-component gradient (Fig. 6) is likely related to the some newly formed siloxane crosslinks between the originally sparse C18 chains and the hydroxyl-terminated molecules at the high-energy end of the gradient. Thus, while the two-component gradient exhibits a lower
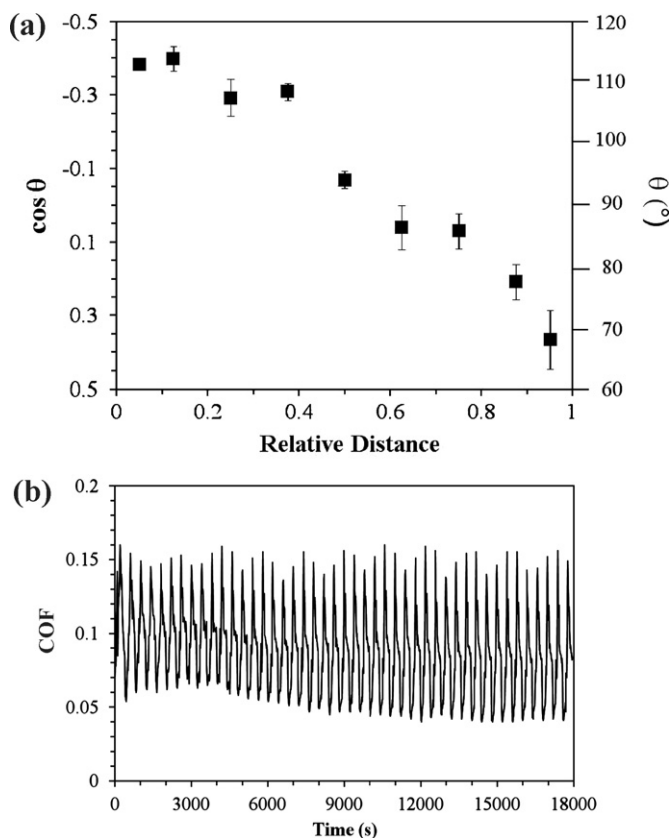
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Fig. 7. (a) The advancing water contact angle (right axis) and its cosine (left axis), which scales as surface energy, measured at relative distances (total distance = 2.0 cm) along the substrate for a two-component gradient monolayer prepared from $C_{18}SiCl_3$ and backfilled with (1-trichlorosilyl undecyl)trichloroacetate, where the trichloroacetyl group was subsequently cleaved to provide hydroxyl termini. (b) Cyclic tribological scanning of the two-component gradient monolayer with a load of 98 mN and a speed of 0.1 mm/s. The cycle time was 400 s.

overall frictional range than the single-component monolayer, it does show a factor of 3 change in COF across the gradient, and its nearly constant performance over at least 5 h indicates that the second component can indeed improve the durability of the gradient with repeated cycling.

4. Conclusions

We have demonstrated a simple and effective approach to assemble single- and dual-component gradient monolayer films of silane precursors onto a silicon substrate by use of an inexpensive peristaltic pump. Characterization of these gradient films by water contact angles and ellipsometric thicknesses confirms gradient formation with a high degree of repeatability. We have shown that the coverage or thickness of a low-energy, single-component, hydrocarbon monolayer is a critical aspect of the frictional response of the film by relating the tribological performance of the gradient monolayer to that of monolayers with known thicknesses. The tribological properties of the gradient monolayer films are strongly dependent on molecular coverage from 0 to 30% but insensitive to higher coverages (30–100%) as the cohesive energy of the chains is sufficient to prevent the probe from contacting the substrate. Sparse monolayer regions are more prone to frictional failure due to exposure of more of the underlying substrate and further enabling the probe tip to impart the normal load to fewer adsorbed molecules to greatly increase the pressure per adsorbate. Two-component monolayer gradients as formed here provide a more robust tribological interface, albeit with a reduced range of

frictional performance, as even a pure hydroxyl-terminated monolayer is significantly more lubricating than an uncoated silicon surface. These films exhibited stable gradient frictional performance for at least 5 h of continuous sliding and a threefold change in the measured COF across the gradient. Collectively, these results provide molecular insight toward the design and fabrication of stable frictional gradients through a convenient trichlorosilane-based monolayer assembly process.

Acknowledgments

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