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Tribological characterization of gradient monolayer films from trichlorosilanes on silicon

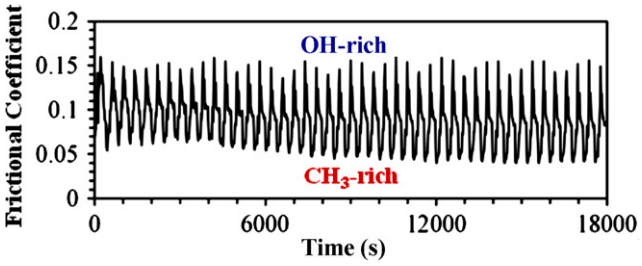
Brandon D. Booth[a], Nathaniel J. Martin[a], Edward A. Buehler[a], Clare McCabe[a,b], G. Kane Jennings[a,*]

[a] Department of Chemical and Biomolecular Engineering, Vanderbilt University, Nashville, TN 37235, United States
[b] Department of Chemistry, Vanderbilt University, Nashville, TN 37235, United States

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



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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

* Corresponding author. Tel.: +1 615 322 2707; fax: +1 615 343 7951.
E-mail address: kane.g.jennings@vanderbilt.edu (G.K. Jennings).

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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.

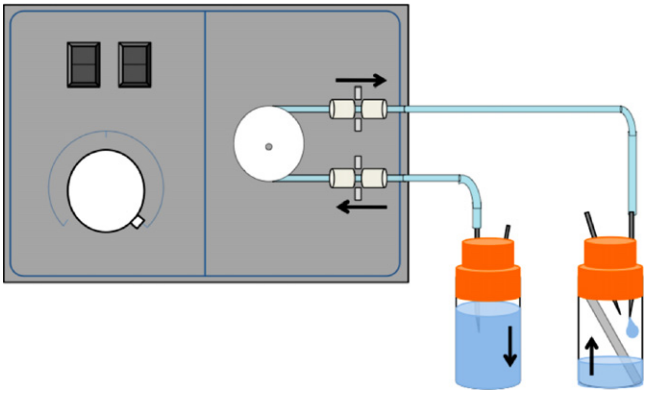

Fig. 1. Schematic illustration of the setup for silane gradient assembly where a peristaltic pump was used to add solvent at 1 mL/min to an initial 0.5 mL starting solution containing 0.5 mM $C_{18}SiCl_3$ and a silicon substrate.

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