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Nanoscale Friction Switches: Friction Modulation of Monomolecular Assemblies Using External Electric Fields

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This paper presents experimental investigations to actively modulate the nanoscale friction properties of a self-assembled monolayer (SAM) assembly using an external electric field that drives conformational changes in the SAM. Such “friction switches” have widespread implications in interfacial energy control in micro/nanoscale devices. Friction response of a low-density mercaptocarboxylic acid SAM is evaluated using an atomic force microscope (AFM) in the presence of a DC bias applied between the sample and the AFM probe under a nitrogen (dry) environment. The low density allows reorientation of individual SAM molecules to accommodate the attractive force between the −COOH terminal group and a positively biased surface. This enables the surface to present a hydrophilic group or a hydrophobic backbone to the contacting AFM probe depending upon the direction of the field (bias). Synthesis and deposition of the low-density SAM (LD-SAM) is reported. Results from AFM experiments show an increased friction response (up to 300%) of the LD-SAM system in the presence of a positive bias compared to the friction response in the presence of a negative bias. The difference in the friction response is attributed to the change in the structural and crystalline order of the film in addition to the interfacial surface chemistry and composition presented upon application of the bias.

Introduction

Self-assembled monolayers (SAMs) are organic molecules which form monomolecular layers spontaneously when a solid substrate is immersed into a solution containing the molecules.1,2 SAMs have been widely used in molecular electronics,3 biosensors,4–14 and microfabrication8–12 and as molecular lubricants for passive tribological control to minimize adhesion and friction in micro/nanoelectromechanical systems (MEMS/NEMS).13–15 Alkanethiols are the most commonly studied SAMs,16 they are relatively easy to prepare, form well-ordered close-packed films, and have been extensively investigated for tribological (friction, wear and lubrication) performance.17–22 Researchers have studied various factors affecting their tribological behavior such as chain length,23,24 terminal group chemistry,19,25–28 pressure,29 humidity,30 packing density,31 and temperature.32 A powerful and robust means of tribological control involves “active” strategies characterized by reversible responses to external stimuli that produce desired changes in the tribological system (surface, lubricant or coating). For example, researchers have investigated the use of an electric field or electric current across an interface3–37 as well as using temperature sensitive polymer films38 to modulate friction at an interface on the macroscale. Liu et al.39 have suggested that friction and wear...
Experimental Section

Materials. (16-Mercapto)hexadecanoic acid (MHA), 4,4'-dimethoxytrityl chloride, dithioerythritol, chlorotrityl chloride, and methoxytrityl chloride, dithioerythritol, chlorotrityl chloride, and silver nitrate were purchased from Sigma Aldrich (St.Louis, MO) and used as received. Gold wires (99.99%) were purchased from Ernest F. Fullam Inc. (New York). Gold-coated (coating thickness ∼200 nm) conductive silicon probes were purchased from Novascan Technologies Inc. (Ames, IA).

Substrate Preparation. Glass slides were cleaned using the following procedure: a 2% RBS-35 detergent solution with 18.2 Mohm water was heated to boiling on a temperature bath and the glass slides were soaked in the boiling solution for 10 min. Then, the glass slides were rinsed with running 18.2 Mohm water for two complete cycles of the water purifier, following which, the glass slides were dried in a laminar flow hood and stored in a desiccant chamber until further use. Cleaned glass slides were coated with 15 nm of Cr (adhesion layer) followed by 200 nm of gold-coated silicon probes for two complete cycles of the water purifier, following which, the substrates were cleaned with 18.2 Mohm water was heated to boiling on a temperature bath and the glass slides were soaked in the boiling solution for 10 min. Then, the glass slides were rinsed with running 18.2 Mohm water for two complete cycles of the water purifier, following which, the glass slides were dried in a laminar flow hood and stored in a desiccant chamber until further use. Cleaned glass slides were coated with 15 nm of Cr (adhesion layer) followed by 200 nm of gold in an e-beam evaporator.

SAM Deposition. A low density 16-mercaptophexadecanoic acid (MHA) SAM system was realized to enable conformational switching as follows. First, (16-MHA) was synthesized as outlined by Lahann et al.42 The synthesis employs a three-step protocol: in the first step, 16-mercaptophexadecanoic acid’s thiol headgroup is treated with trifluoroacetic acid (TFA) to result in removal of the ester group and formation of a low density monolayer of 16-mercaptophexadecanoic acid (MHA). Note that due to the low density, the film will have a slightly disordered structure rather than the ordered structure shown.

Characteristics of Langmuir–Blodgett (LB) films can be controlled and potentially improved using external electric fields. Park et al.40 and Qi et al.41 have shown that friction can be electronically controlled by forward/reverse biasing between a conductive AFM probe and a semiconductor surface. Lahann et al.42 showed that electric fields will have negligible effect on close-packed monolayer systems and developed a switching surface with loosely packed SAMs. They postulated that, in order to obtain a SAM system for conformational switching, sufficient spatial freedom for each molecule to do so must be established. They realized a low-density SAM using thiols of (16-mercaptop)hexadecanoic acid (MHA) because of its established self-assembly on gold surfaces and its hydrophobic chain and hydrophilic end-group combination. In this paper, we report our initial investigations on the possibility of using external electric fields as a means to actively control the friction response of a low density MHA film via atomic force microscopy experiments. This kind of a “friction switch” could potentially be employed in micro/nanoscale devices to control fluid flow (in microfluidics) or sliding of movable components (micro/nanoelectromechanical systems).

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Ellipsometry Measurements. Ellipsometry measurements were used to determine the thickness of the monolayer before and after the treatment with TFA. These measurements were carried out using an automated optical system (MultiSkop, Optrel GbR, Berlin, Germany). For the ellipsometry measurements, only half of the glass-slide coated with gold was exposed to the MHA SAM, thus producing a substrate with the SAM only on half of the substrate. Figure 3a shows the
thickness (height) of the monolayer from ellipsometry measurements performed in a line across from the gold side of the sample to the MHAE side. The average thickness of the MHAE layer (with reference to zero thickness of gold) was about 22.47 ± 0.23 Å. After this measurement, the whole substrate was incubated in the 50% TFA solution in ethanol for 2 min. Figure 3b shows the thickness of the monolayer after the acid treatment. The average thickness (height) of the MHA layer (with reference to gold) was about 14.10 ± 0.29 Å. In the former case, the larger thickness indicated that the MHAE monolayer must be close-packed and standing upright because of the presence of bulky ester group. Acid removal of the ester group creates a loosely packed layer of MHA in which the molecules have sufficient space to change conformation or bend in order to reduce the surface energy and result in a lesser thickness (height).

The SAM substrates were prepared freshly prior to each experiment—in between runs, the samples remained in the nitrogen atmosphere within the AFM. These substrates have been shown to be chemically stable under ambient conditions, and it is reasonable to expect no significant oxidative degradation or moisture adsorption.

**Atomic Force Microscopy.** Friction and pull-off force experiments were carried out using a Dimension 3100 (Nanoscope IV, Veeco Instruments, Santa Barbara, CA) AFM under a nitrogen atmosphere (10 ± 2% relative humidity) to minimize effects of adsorbed water vapor. Commercially available rectangular Si cantilevers (made conductive by a 200 nm gold coating throughout) were used for all measurements. The normal spring constant of the cantilever was calibrated using the reference lever technique described by Torii et al. AFM force-displacement curves provided the pull-off (adhesive) force, between the Si tip and the sample. Friction force scans were performed at a 90° scan angle on a 1 × 1 μm scan area with a scanning speed of 2 Hz. The friction response of the tip on a sample was taken to be the difference between the lateral deflection values of forward and reverse scans of a given scan line (i.e., from the friction loop of a scan line). The friction value thus noted is a measure of the friction force. This method is commonly used to eliminate contributions from nonfriction sources. Friction force data presented are averages of six measurements at multiple sample locations. To help ensure that the observed friction response was not affected by change in tip radius, the radius of the tip was characterized before and after the experiments using a commercially available tip characterizer sample TGT01 (Mikromasch). The images were then analyzed using commercial software (Image Metrology) to calculate the tip radius. The tip profiles are generated using a MATLAB code. Using this methodology, we found that the tip radius did not change appreciably (observed change was less than 7%) during our experiments.

![Figure 2. XPS measurements showing intensities of elements before (black) and after treatment (white) of the MHAE self-assembled monolayers (SAMs) (on a silicon substrate) with trifluoroacetic acid.](image_url)

![Figure 3. Thickness measurements (using ellipsometry) of the MHAE thin film (a) before treatment with TFA and (b) after treatment with TFA. The TFA treatment removes the bulky ester group, which results in a low density carboxylic acid-capped SAM system and hence a lower thickness.](image_url)

Results and Discussion

In order to study adhesion and friction of the SAM system in the presence of an electric field using an atomic force microscope, the probe/cantilever (standard Si$_3$N$_4$ probes coated with a 200 nm thick gold layer) was connected to ground while a positive or negative bias (with respect to the ground) was applied to the metallic sample holder as shown in Figure 4. The SAM substrate was attached to the sample holder using a conductive copper tape. This arrangement results in the contact area between the probe and sample being completely enclosed in an electric field during application of bias for subsequent friction and adhesion measurements. Data obtained are presented as averages of six measurements at multiple sample locations.

Figure 5a shows a plot of the pull-off forces measured on the MHA monolayer as a function of sample bias (0, +10, and −10 V). A monolayer thickness of ∼14 Å (from ellipsometry measurements) will correspond to a field strength value of 0.71 V/Å for an applied voltage of 10 V. This estimate assumes no other layer is present on the surface (such as moisture). As a comparison, Pertsin et al. performed Monte Carlo simulation studies to show that DC fields on the order of 1 V/Å can substantially change the equilibrium configuration of an ethylene-glycol terminated alkanethiol SAM. In particular, the oxygen atoms of the terminal group were either buried or exposed depending on the polarity of the applied field. In our experiments, some bending of the force curve (Figure 5b) was observed during application of bias, which corresponds to deflection caused by electrostatic attraction. The difference between unbiased and biased deflection values (obtained from a force curve as distance between snap in point and the far field zero deflection position of the cantilever, represented by the dotted line in Figure 5b) would be the amount of deflection ($d_{bias}$) due to electrostatic attraction. The normal load equivalent to this intrinsic electrostatic attraction ($NL_{bias}$) at a particular bias can then be calculated by multiplying the deflection by the cantilever spring constant, $k$ as $NL_{bias} = d_{bias}k$. This additional load is taken into account while reporting normal load numbers for friction experiments.

The pull-off force is higher when a negative bias is applied than when a positive bias is applied. This difference was observed for voltages in the range of 6–10 V. Measurements below 6 V did not yield appreciable differences between positive and negative biases. Experiments at voltages higher than 10 V (and hence field strength) resulted in observable damage to the SAM surfaces. It is expected that when a negative bias is applied to the substrate, the resulting field will repel the carboxylic end-group and keep the molecule in a more or less upright position as shown in Figure 6a. In this position, during a force curve experiment, these hydrophilic end groups will interact with the hydrophilic gold-coated SAM. Thus the behavior of the adhesive force is indicative of the presented surface chemistry as a function of bias. This behavior is consistent with the wettability data reported by Lahann et al. as a function of bias.

Our initial expectation of the friction response as a function of sample bias was to match that of the pull-off force; that is, it would increase as the hydrophilicity of the presented end-group chemistry increased as has been shown for densely packed monolayers. However, as seen in Figure 7, which shows the friction response of the low-density MHA substrate with a gold-coated conductive Si probe at 0 V, +10 V and −10 V bias (applied to the sample), this was not the case. The data show that friction response increases with an increase in normal load in all three cases in a slightly nonlinear fashion. This is commonly observed

![Figure 4](image-url)  
**Figure 4.** Schematic of the experimental setup for providing a bias between the grounded atomic force microscope (AFM) probe and the self-assembled monolayer (SAM) sample. The cantilever and probe are made of conductive silicon with a 200 nm gold coating.
At voltages below 6 V, no appreciable increase in friction due to the positive bias was observed, and the friction response reverted back to levels comparable to the unbiased condition. Upon removal of the applied bias, the friction response for the positive bias is much higher compared to the negative bias condition. The bias effect is illustrated by the fact that the friction response for the negative bias is almost equivalent to the 0 V bias case at lower loads and a little lower at higher loads. This trend was observed at applied voltages of 6–10 V. Within this range, the observed increase in friction due to the positive bias was observed to be completely reversible. That is, upon removal of the applied bias, the friction response reverted back to levels comparable to the unbiased condition. At voltages below 6 V, no appreciable difference in friction was observed (with respect to unbiased condition). At voltages higher than 10 V surface damage was observed after experiments. As a comparison, control experiments on closely packed (crystalline) SAMs of MHA and hexadecanethiol showed no change in friction response upon application of voltage in the range of 6–10 V, which confirms observations of Lahann et al., that densely packed monolayers do not have sufficient space to undergo conformational change.

Upon further investigation of the contribution to the friction force in SAM systems, it became evident that the structural order of the monolayers is a critical factor in addition to presented surface chemistry. Note that, in the absence of bias, the loosely packed monolayer will be some form of disorder compared to a tightly packed monolayer. In the case of the negative bias, though the molecules are spaced apart, they are relatively ordered and well-structured. When a positive bias is applied, the bending of the molecules toward the substrate further compromises the structural order of the monolayer. Lee et al. have shown that the differences in packing densities and crystalline order between an alkanethiol and spiroalkanedithiol gave rise to differing friction responses. Specifically, spiroalkanedithiol did not seem to have the ordered (\(\sqrt{3} \times \sqrt{3}\) R30°) structure and gave a higher friction response than the normal alkanethiol. Their work suggested that, when the tip traverses across the carbon backbone, which is commonly the case in disordered films than for ordered film structure, an increase in the van der Waals interaction occurs, resulting in increase in shear strength per unit area and hence increased friction force. Applying this argument to our friction data, the relatively disordered structure of the film under positive bias will work to increase the friction response, compared to a relatively ordered structure. Whereas in the case of negative bias, the relatively ordered structure of the film will work to decrease friction response. These effects are opposite to the effect of interfacial surface chemistry (hydrophilicity). The fact that the observed friction does increase dramatically for the positive bias case compared to the negative bias case suggests that the contribution from the ordering of the film outweighs the contributions from the presented chemistry. It should be noted that the potential regime in which we observed friction differences (6–10 V between probe and substrate) was significantly different from that of Lahann et al., who observed conformational changes of an LD-SAM in the more narrow potential range of –1.1 to +0.700 V (vs SCE). Evidence suggests that higher

For carefully conducted friction experiments at the nanoscale and is representative of the contact area dependence of friction.

The bias effect is illustrated by the fact that the friction response for the positive bias is much higher compared to the negative bias throughout the load range employed, which is counter to the trend seen for pull-off force. At an applied load of 40 nN, friction response for the positive bias condition is almost 3 times higher than for the negative bias condition. The friction response for the negative bias is almost equivalent to the 0 V bias case at lower loads and a little lower at higher loads. This trend was observed at applied voltages of 6–10 V. Within this range, the observed increase in friction due to the positive bias was observed to be completely reversible. That is, upon removal of the applied bias, the friction response reverted back to levels comparable to the unbiased condition. At voltages below 6 V, no appreciable

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**Figure 6.** Schematic showing interaction of the AFM probe with the low density MHA monolayer when a negative bias (top) and a positive bias (bottom) is applied. During negative bias, the molecule is relatively well ordered and presents the hydrophilic end (top) and the hydrophobic end (bottom) is applied. During negative bias, the molecule is relatively well ordered and presents the hydrophilic end whereas when a positive bias is applied, the molecule exposes more of the hydrophobic backbone and compromises the ordered structure.

**Figure 7.** Data from AFM friction experiments on the MHA low density SAM for various applied fields (0, +10, and –10 V).

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potentials may result in desorption of thiols. However as noted previously, we did not observe any surface damage for our applied voltage and therefore we believe no desorption occurred. We think it is reasonable to assume that the field strength in our experiments may be similar to those of Lahann et al. It is clear that further investigations are needed to better understand the exact mechanisms of the observed phenomenon. We are currently employing computational studies to further understand the nature of the conformational changes in the SAM system as well as their predicted impact on friction properties.

**Conclusions**

In conclusion, we have demonstrated that an external electric field can be used as a friction switch for a low-density thiol-tailed hexadecanoic acid SAM film on a gold substrate. The low density allows sufficient space for field-induced conformational changes to occur as a result of attraction/repulsion between the polar end group and the substrate. AFM friction experiments, in the presence of a positive bias show a higher friction response than a negative bias upon application of load. This bias dependency of the friction was observed for applied voltage magnitudes of 6–10 V, which correspond to field strengths of approximately 0.43–0.71 V/A. This difference in friction response upon changing the polarity of the field is attributed to the changes in the structural and crystalline order of the film. Further studies to verify this hypothesis are being undertaken. It is expected that these efforts will lead to strategies that can harness conformational changes of film assemblies for tunable friction behavior.

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