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Tribological Properties of Self-Assembled Monolayers on Au, SiO_x and Si Surfaces

H. I. Kim[a], V. Boiadjiev[b], J. E. Houston[a], X. –Y. Zhu[b], J. D. Kiely[c]
[a] *Sandia National Laboratories, Albuquerque, New Mexico 87185-1421*
[b] *Department of Chemistry, University of Minnesota, Minneapolis, MN 55455*
[c] *Seagate Research, Pittsburgh, PA 15203-2116*

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Abstract

Using interfacial force microscopy (IFM), the tribological properties of self-assembled monolayers (SAM) on Si surfaces produced by a new chemical strategy are investigated and compared to those of "classical" SAM systems, which include alkanethiols on Au and alkylsilanes on SiO_x. The new SAM films are prepared by depositing *n*-alkyl chains with OH-terminations onto Cl-terminated Si substrates. The chemical nature of the actual lubricating molecules, *n*-dodecyl, is kept constant in all three thin film systems for direct comparison and similarities and differences in tribological properties are observed. The adhesion strength is virtually identical for all three systems; however, frictional properties differ due to differences in film packing. Differences in the chemical bonds that attach the lubricant molecules to the substrate are also discussed as they influence variations in film wear and durability. It is demonstrated that the new SAM films are capable of controlling the friction and adhesion of Si surfaces as well as the classical SAMs in addition to providing a greater potential to be more reproducible and more durable.

1. Introduction

Organic monolayer films are becoming increasingly important as boundary lubricants in a variety of applications where molecularly thin lubricants are desired. One of the industrial applications that require the use of thin film lubricants is the newly emerging microelectromechanical systems (MEMS) [1]. Currently, SAMs of alkylsilanes are being considered in MEMS to control adhesion and friction between micrometer-sized moving parts that are made of silicon. Although they have been shown to successfully passivate and lubricate Si

surfaces [2], they possess numerous limitations that are intrinsic to the chemistry of film deposition. First, silicon surfaces must be oxidized in order to react with the trichlorosilane head group of the precursor and the amorphous nature of the oxide layer may contribute to the amorphous packing arrangement of the deposited film, which can adversely affect the frictional properties. Second, in competition with monolayer formation, the alkyltrichlorisilane precursors can polymerize or form other microstructures, such as reverse micelles, in the liquid phase, resulting in the deposition of large clusters on the substrate. Once formed, these clusters cause premature failure of devices and are difficult to remove or make uniform. Third, the film deposition process is extremely sensitive to the amount of water present in the deposition medium; water is a necessary part of the reaction that binds the precursor to the substrate, but it is also what triggers polymerization or micelle formation in the solution. This makes the deposition process very difficult and irreproducible. Fourth, even after initially forming a good and uniform monolayers of alkylsilane, they have been found to degrade when exposed to high humidity [3]. Although not completely understood, it is likely that the monolayer is weakly adsorbed on the surface via mostly H-bonding, instead of covalent linkage. Water can also break the Si-O-Si linkage between the lubricant molecules and the substrate (R-Si-O-Si) [4].

Obviously, there is considerable motivation to develop a thin film system that is more reproducible and more durable under various environmental conditions including high humidity. Here, a new type of SAM preparation strategy is discussed which involves the reaction of long-chain alcohol molecules with the silicon surface that has been pre-chlorinated [5]. This results in a SAM that has the same lubricant molecules (*n*-alkyl chains) that are directly attached to the Si surface via covalent -C-O-Si linkages.

In this study, the tribological properties of SAM films produced by this new method on the silicon surface is explored and compared to those of classical SAMs that have been studied more extensively. Also, their potential for enhanced reproducibility and durability is discussed. The classical SAMs discussed here are alkanethiols on Au and alkylsilanes on SiO_x. SAMs of alkanethiols on Au have often been studied as "model" boundary lubricants because of the crystalline packing structure that is well known and reproducibly obtained [6-10]. SAMs of alkylsilanes have also received considerable attention for their frictional properties [11-13]. Alkanethiol SAMs on Au, alkylsilane SAMs on SiO_x and the new SAM (alcohols on Cl-Si) are observed to have distinctively different frictional properties despite the fact that the actual lubricant molecules (*n*-dodecyl) are exactly the same in all cases. This difference is explained in terms of the differences in the packing order of the alkyl chains. The different chemical bonds that bind the lubricant molecules to their respective substrate in each system are discussed in regards to their potential durability and wear properties.

2. Experimental Details

The adhesions and frictional properties of the organic thin films presented here are measured using interfacial force microscopy (IFM). This instrument, which has been described in detail elsewhere [14], is distinguished by its use of a feedback sensor to ensure that sensor compliance (which adds to the complexity and uncertainly of the measured forces in most deflection based experiments) does not exist. Also, the simplistic geometry of the sensor allows the quantitative measurement of interactive forces between the probe tip and the sample surfaces.

The IFM sensor consists of a capacitor common plate suspended above two capacitor pads by torsion bars bisecting the long axis. A tip is placed on one end of this plate such that when a force is applied to the tip by the interacting sample surface, it will rotate about the torsion bars to off-balance the differential capacitance. The deflection is measured by a RF bridge-circuit and the resulting signal is fed to a controller, which applies DC voltages to the capacitor pads in order to balance the deflection. The resulting voltage from the controller output is directly related to the magnitude of the force acting on the tip without any sensor motion. The relationship between the voltage and force is dependent only on the capacitor geometry and is easily calibrated. In addition, the force-feedback sensor will balance any force applied to the tip which produces a torque about the torsion-bar axis and this is the basis for making lateral force measurements in the friction mode, as described below.

Friction forces are measured in a constant torque mode by modulating the tip/sensor assembly laterally along a direction perpendicular to the torsion-bar axis and monitoring the torque modulation due to lateral tip-sample interaction. Since the tip/sensor assembly is modulated at a specific frequency (typically at 100 Hz), any frictional force present between the tip and the sample will cause the torque on the sensor to modulate, thus, modulating the measured force at the same frequency. A dual channel lock-in amplifier is used to measure the amplitude of this force modulation at the given frequency. In summary, normal forces are measured by balancing the average torque on the sensor caused by tip-sample interaction in the normal direction and friction forces are measured by balancing the modulating sensor torque arising from lateral tip-sample interaction. These are measured simultaneously as the tip approaches the sample surface at a constant rate from a few hundred Å away. After reaching a certain level of normal force (or friction force), the tip is withdrawn at the same rate. The slope of the friction force vs. normal force plot is often found to be relatively linear and is referred to as the friction coefficient (μ), which is a characteristic frictional property of a given sliding interface [15].

Dodecanethiol (C_{12}-SH) monolayers were assembled by submersing Au(111) surfaces (flame-annealed 99.99% pure Au wire [16]) into a 1 mM ethanol solution of dodecanethiol [$CH_3(CH_2)_{11}SH$] for 24 h. Then the samples were rinsed in ethanol and dried in N_2. Dodecyltrichlorosilane (C_{12}-$SiCl_3$) films were prepared from $CH_3(CH_2)_{11}SiCl_3$ solution on the oxide-covered Si(100) wafers (SiO_x) [17]. Dodecanol (C_{12}-OH) films were prepared by reacting dodecanol [$CH_3(CH_2)_{11}OH$] with Cl-terminated Si(111) [18]. The probe tip used in this study was electrochemically etched tungsten wire that had radius of ~ 2000 Å. The same tip was used for all data presented here for the purpose of direct comparison. Experiments were conducted in air at relative humidity levels of less than 20%.

3. Results and Discussion

Shown in Fig. 1 is plot of the friction force measured as a function of applied load for a C_{12}-SH film on Au(111) and a C_{12}-$SiCl_3$ on SiO_x. Consistent with previous studies, a very low adhesion (~ 50 nN) and low friction ($\mu = 0.003$) is seen for C_{12}-SH/Au. The μ of 0.003 is an extremely low friction coefficient and is due to the close-packed arrangement of *n*-dodecyl backbone chains, which arises from the $(\sqrt{3} \times \sqrt{3})R30^\circ$ adsorption geometry of the sulfur head groups on the Au(111) lattice and the 30° tilt angle of the alkyl chains [10]. It has been demonstrated in the past that similar *n*-alkanethiol films can withstand up to several GPa of pressure in the normal direction while still exhibiting such a low fiction coefficient [19, 20]. For a freshly prepared *n*-hexadecanethiol on Au(111), wear and degradation of the film are not observed up to about 3.7 GPa. However, it has been observed that alkanethiol films oxidize and age when exposed to ambient air due to the oxidizing specie, ozone [21, 22]. Ozone attacks the thiolate bond to the Au, forming sulfonate head group which is only weakly adsorbed to the Au surface. This causes defects due to desorption of the alkyl backbone molecules [23, 24]. This, in turn, reduces the degree of packing order of these films [21, 25] and opens up more vibrational, rotational, and gauche relaxation modes under a sliding contact, resulting in higher energy dissipation and higher friction [12]. The friction coefficient of an aged film (for 1.5 months) is measured to be about 0.075 [19, 20]. Although this is a dramatic increase from that of the freshly prepared films, it is still relatively a low friction coefficient. Also, virtually no increase in adhesion was observed on the aged film compared to the fresh film. The low adhesion and frictional properties of alkanethiol films make them attractive boundary lubricants except for the fact that they adsorb on gold surfaces instead of on Si or SiO_x surfaces. Since the majority of MEMS devices are made of silicon, their use in MEMS is limited because selective parts of Si surfaces must be first coated with a thin layer of gold.

For the lubrication of Si surfaces, SAMs of alkylsilanes have been the most popular choice [1, 26]. Figure 1 shows a direct comparison of adhesion and friction controlling capabilities of C_{12}-$SiCl_3$ on a SiO_x surface with respect to those of C_{12}-SH on Au(111). The friction coefficient (0.012) is higher for the alkylsilane SAM compared to that (0.003) of alkanethiol SAM of the same chain length. This is attributed to the fact that alkylsilane film on SiO_x is less well ordered. The ordering of alkylsilanes has been described as being liquid-like, short range order partly due to the amorphous nature of the substrate (SiO_x) and partly due to cross-linking of the Si head groups of the alkylsilane molecules with the neighboring molecules. However, there remains much uncertainty about the extent of this cross-linking and the details of the bonding of the alkyl chains to the oxide substrate [27]. In fact, it is now realized that only a few of the alkyl chains are chemically bonded to the substrate and to the neighboring chains [28]. Figure 2 shows a schematic representation of the likely film structures of the alkylsilanes on SiO_x and alkanethiols on Au(111); the alkylsilane SAM is depicted as being more disordered. Nevertheless, the friction coefficient (0.012) of the C_{12}-$SiCl_3$ is good for the purposes in MEMS and the force of adhesion is also very low (~ 50 nN) as shown in Fig. 3, which demonstrates that an alkylsilane SAM significantly reduces the adhesive strength of a SiO_x surface.

The major problem with the alkylsilane SAMs, however, is the fact that the reproducibility is very poor as it critically depends on the water content in the deposition medium and on substrate preparation. Water is a necessary part of the reaction that binds the Si head group to the substrate as well as to the neighboring Si head groups via Si-O-Si linkage according to the generally accepted reaction [4]:

$$R\text{-}SiCl_3 + H_2O \leftrightarrow R\text{-}Si(OH)_3 + HCl\uparrow \leftrightarrow R\text{-}Si(OSi)_3 + H_2O. \qquad (1)$$

Too much H_2O polymerizes the alkylsilanes, resulting in a non-uniform film. If no water is present, the chemical bonding does not take place. It has been found to be very difficult to control the amount of water both on the substrate and in the deposition medium. Another problem with the alkylsilanes is that the film is not stable in high humidity (> 80%) [3]. A uniform layer of alkylsilanes can transform into a non-uniform film as the Si-O-Si linkages are broken and the alkyl chains are detached from the substrate [4, 29]:

$$R_3\text{–}Si\text{–}O\text{–}Si\text{–}R_3 + H_2O \leftrightarrow 2R_3Si\text{–}OH. \qquad (3)$$

The new SAM films investigated in this study offer the potential for enhanced reproducibility and stability since alkyl chains are chemically bonded to the substrate by a different linkage than Si-O-Si. Dodecanol (C_{12}-OH) is reacted with a silicon surface that is terminated with a chlorine layer. This results in a SAM of dodecyls that are *directly* bonded to the Si surface atoms via C-O-Si linkage [5]. As indicated by the schematic representation in Fig. 4, this film does not have cross-linking between neighboring chains and it is expected that every alkyl chain is chemically bonded to the substrate, unlike in the alkylsilane case. Figure 5 shows the friction vs. load plot for the dodecanol SAM on Si(111) surface. It shows that the friction coefficient (0.013) is similar to that of alkylsilanes on SiO_x, indicating of a good lubricant. The adhesion (~ 50 nN) is basically the same as alkylsilanes and alkanethiols. Therefore the dodecanol SAMs would be good films for controlling friction and adhesion of silicon surface. In fact, they have been successfully [30] applied to cantilever beam array (CBA) test structures manufactured by MEMS technique [31]. The details of this work will be discussed elsewhere.

Although, 0.013 is a very low friction coefficient, it is higher than what is expected for a closely packed film. It was initially expected that R-OH on Cl-Si surface would pack more closely than alkylsilanes since there is no cross-linking between head groups. Closer packing would lead to a higher degree of film order and lower friction. However, the higher than expected friction coefficient on the dodecanol film suggests that the film is actually not packed more closely than alkylsilane films. This suggestion is supported by film density measurements carried out on the dodecanol SAM using the low angle X-ray reflectivity technique, which indicated that the density of alkyl chains in the dodecanol SAM is about 85% of that in a close-packed alkyl assembly [32]. The reason for the loose packing is due to the lattice mismatch of the Si(111) substrate and the dodecanol molecule; the surface unit cell area on unreconstructed Si(111) surface is 12.8 $Å^2$/atom (too small to support a monolayer of SAM) and the surface area per alcohol chain within the monolayer is estimated to be ~ 25.4 $Å^2$. So, it is likely that they bind to every other Si atom at best [33], although the fundamental properties of the adsorption geometry on the Si substrate are not completely understood at this time.

The potential advantages of the R-OH SAM over the alkylsilane SAM involves their reproducibility and durability. The process of coating the chlorinated Si surface with R-OH requires that the deposition medium be completely free of water, since water would react with chlorines on the surface, reducing the number of binding sites. Thus, this process is still "sensitive" to water content. However, it is easier to eliminate water in the reaction vessel than to try to maintain the "right" amount (which is often undetermined in the case of alkylsilane SAM formation). Consequently, the reproducibility of forming R-OH SAMs is expected to be better. Also, the R-OH films have a potential to be more durable since essentially all the alkyl chains are expected to be chemically bonded to the substrate. The use of a chlorinated Si substrate allows deposition of amine terminated alkyl chains (R-NH2) to yield a SAM where each alkyl chain is chemically bonded to the Si substrate via *two* silicon nitride bonds [5, 34]. These new monolayers may offer enhanced durability and inertness to severe environmental conditions, including humidity. Considerably more work is needed to realize this potential and it is currently in progress.

4. Conclusion

Reported here are the results corroborating the suggestion that tribological properties of self-assembled alkyl chains are closely related to their packing arrangements and the stability of their chemical bonds to the substrate [12, 19, 20]. Therefore, SAMs of the same alkyl chains and with the same chain lengths exhibit different frictional characteristics on different substrates. However, the adhesion to all the thin films discussed here are observed to be essentially identical, since they are all terminated by chemically inert methyl groups. SAMs of alkanethiols on Au(111) have the lowest friction coefficient among them and alkylsilanes films on SiO_x surfaces exhibit higher friction coefficient because of the disordered nature of the film. Although it still is a good lubricant for silicon surfaces, poor reproducibility and poor durability in humid environment encourages the development of SAMs for silicon surfaces. A great potential is seen in long-chain alcohols that are self-assembled on pre-chlorinated Si surfaces by altering the chemical linkage of the alkyl chains to the Si substrate. The advantages of this new SAM preparation method include easier process control, enhanced reproducibility and the fact that essentially all alkyl chains are bonded directly to the Si atoms on the substrate.

5. Acknowledgement

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7. Figure Captions

Figure 1. Friction vs. load plot for a C_{12}-SH SAM on Au(111) (closed circle) and C_{12}-$SiCl_3$ SAM on SiO_x (open circle). The friction coefficient (μ) of the C_{12}-$SiCl_3$ film is shown to be about 4 times greater than that of the C_{12}-SH film. However, the adhesion of both films are essentially the same at about 50 nN.

Figure 2. The likely film structures are schematically represented for C_{12}-$SiCl_3$ SAM on SiO_x (left) C_{12}-SH SAM on Au(111) (right). The higher friction coefficient of the alkylsilane films shown in Fig. 1 is due to the higher degree of the film disorder, which arises from the amorphous nature of the substrate and unknown extent of the chemical bonding of the head group to the substrate and to the neighboring head groups.

Figure 3. Normal force measurement on a bare SiO_x (closed circle) and a C_{12}-$SiCl_3$ SAM on SiO_x (open circle). Shown by the magnitude of the negative normal force, the adhesive strength of the surface is significantly reduced when coated with an alkylsilane film.

Figure 4. The schematic representation of the R-OH self-assembled on a chlorinated Si surface is shown. After the reaction is complete, each alkyl chain is bound directly to the Si surface atoms by C-O-Si linkage and no cross-linking between chains are expected. However, the alkyl chains are shown to occupy every other Si atom due to the lattice mismatch with the substrate.

Figure 5. Friction vs. load is plotted for C_{12}-OH SAM on Cl-Si surface. The friction coefficient is similar to that of alkylsilane SAM, indicative of a well-lubricated interface. The adhesion (~ 50 nN) is essentially the same as for alkylsilane SAM on SiO_x and alkanethiol SAM on Au(111).

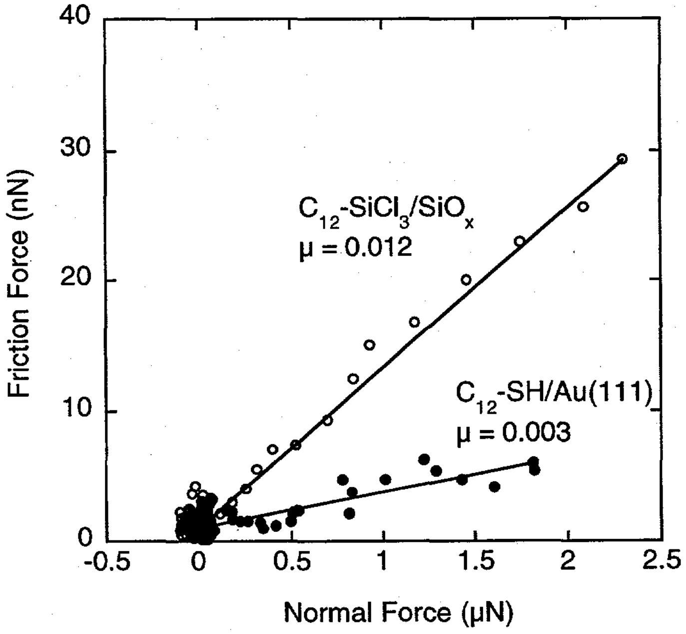
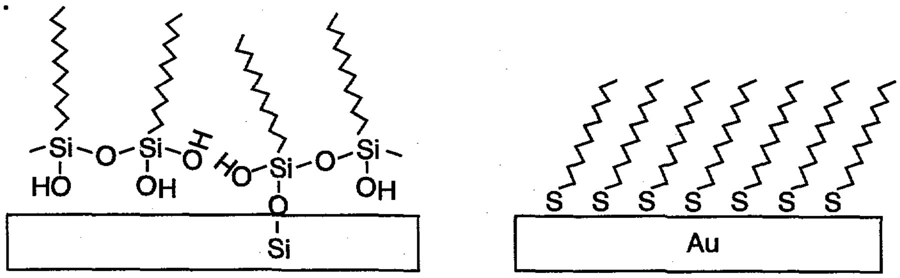


Figure 1, Kim et al.



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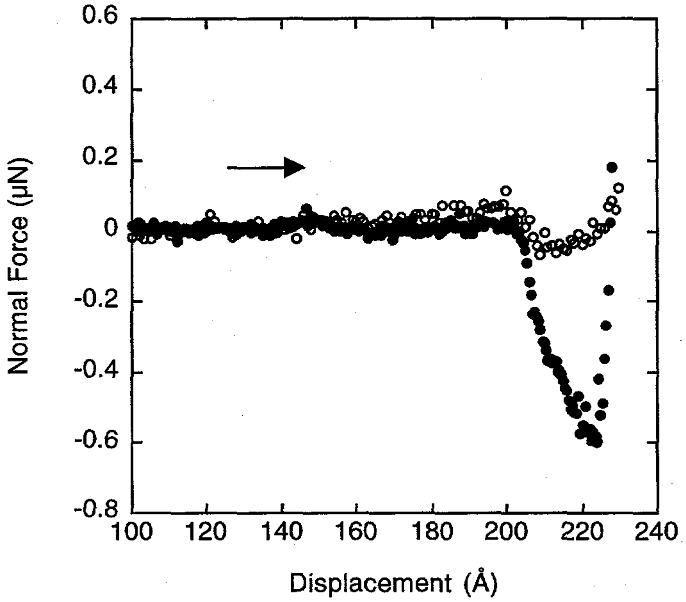

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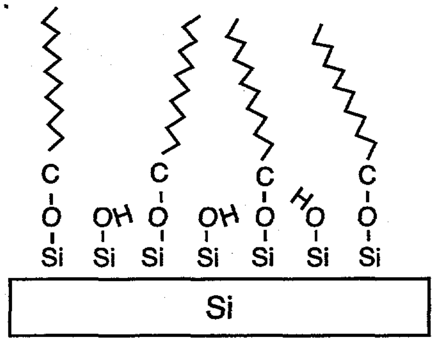

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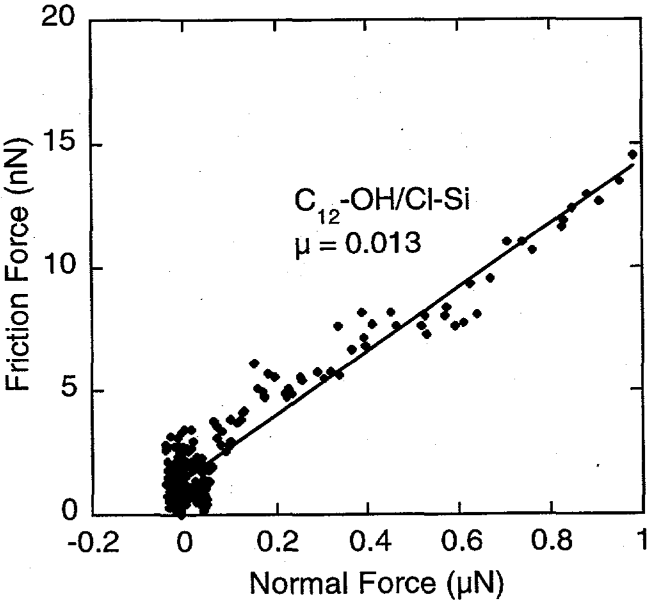

Figure 5, Kim et al.