Effect of self-assembled monolayer film order on nanofriction

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Self-assembled monolayers (SAMs) have increasingly been explored as potential protective films in devices against friction and adhesion. However, detailed characterization of the monolayer film structure is difficult. This article utilizes a combination of near edge x-ray absorption fine structure (NEXAFS) spectroscopy and Fourier transform infrared (FTIR) spectroscopy to determine the film structure in order to explain the observed nanofriction measurement results. A series of n-alkyltrichlorosilane self-assembled monolayer films with various chain lengths (C5–C30) was prepared on silicon (100) surfaces. Nanofriction measurements were conducted using an atomic force microscope. Results showed that the lowest friction was obtained with a C12 film with higher friction values observed for C5 and C30 films. To explain these observations, the x-ray absorption technique NEXAFS was used to quantitatively measure the surface molecular orientation (order) of these films. It was observed that C12, C16, and C18 films were highly ordered with a molecular orientation of the carbon backbone nearly perpendicular to the surface. C5 and C30 films were less oriented and C10 film showed partial orientation. FTIR spectra suggested that these films possessed different degrees of order. This combination of molecular orientation and order supports and confirms that nanofriction results were heavily influenced by the order and structure of these films. [DOI: 10.1116/1.2204920]

I. INTRODUCTION

Self-assembled monolayers (SAMs) are formed by functionalized linear alkyl molecules attaching themselves to an energetically uniform surface to form thermodynamically stable and closely packed structure.1 The order of the film structure is controlled by the uniformity of the adhesive bonds between the molecules and the surface and the cohesive forces among neighboring molecules. Because of the molecular scale of these films, detailed characterization of the order and structure of SAMs is difficult to achieve. At the same time, SAMs have been widely used in many applications and are emerging as a key tool in microelectronics, nanoelectromechanical system (NEMS) fabrication, and device patterning.2

On ideal surfaces, SAMs are self-limiting to a monolayer and this characteristic renders its use as model surface films for further processing and manipulation as hydrophobic films, barrier films, and organic spacers. With proper modifications, SAMs can be used as molecular recognition biosensors, lubricating films in digital mirror devices, and deepen surface patterning of organic molecules.3

Another emerging application for SAMs is barrier films for devices to control adhesion and hydrophobicity of the components. In microelectromechanical system (MEMS) application, SAMs have been used as the lubricating film to reduce friction between moving parts, for example, SAMs are used in digital mirrors image chips to prevent adhesion and lubricate the sliding parts.4

We have conducted friction measurements on a series of trichlorosilanes with different chain lengths on gold surfaces and found that the friction is the lowest for the C12 silane film with intermediate chain length. Longer chain lengths have shown higher friction levels.5 This result is contrary to the long-established observation of longer chain length producing lower friction in macroscale experiments.6 This article examines the structure and order of these films in an attempt to explain the friction results. Detailed experimental results of the friction measurements will be presented elsewhere.6

II. ORDER AND STRUCTURE OF SELF-ASSEMBLED MONOLAYER FILMS

The order of the film structure is controlled by the packing density of the molecules and the spacing of the molecules on the surface. Since we cannot measure directly the packing density of the molecules and if the surface is energetically uniform, then the defect population can be linked to the degree of molecular orientation or alignment in a particular direction on the surface. The molecular orientation of alkanethiol SAMs on gold surfaces has been studied,2,8 but the results have not been linked to the nanomechanical properties (such as frictional characteristics) of the films.

Synchrotron based near edge x-ray absorption fine structure (NEXAFS) is a versatile tool to measure quantitatively the degree of molecular orientation of SAMs.6,11 NEXAFS is a nondestructive spectroscopic method in which soft x-rays are absorbed causing resonant excitations of core K or
L shell electrons to unoccupied (antibonding) molecular orbitals. The initial-state K-shell excitation gives NEXAFS its elemental specificity, e.g., carbon, oxygen, and substrate copper, while the final-state unoccupied molecular orbitals give NEXAFS its bonding or chemical selectivity. Linearly polarized soft x-rays can be exploited to measure bond orientation in a film. The NEXAFS resonance intensities vary as a function of the direction of the incident polarized x-ray relative to the axis of the $\sigma^*$ and $\pi^*$ orbitals. This variation in resonance intensity allows a measurement of the average molecular orientation of the alkyl chain in $n$-alkyltrichlorosilane ($R$-SiCl$_3$ where $R$ contains 5–30 carbon atoms) SAMs with respect to the surface. Due to high surface sensitivity, molecular orientation sensitivity, rapid data acquisition, and analysis, the NEXAFS technique affords clearer molecular ordering information than infrared reflection or absorption spectroscopy. Recently, NEXAFS has been applied to determine the orientation of organized assemblies of organic molecules, such as self-assembled monolayers of oriented fatty acids, and surfaces of thin polymer films and has evolved into a routine synchrotron soft x-ray spectroscopic tool. In the present study we report molecular orientation and structure utilizing NEXAFS of alkyltrichlorosilane SAMs of various carbon lengths on silicon. The results from NEXAFS were also compared with other qualitative techniques such as Fourier transform infrared (FTIR) and atomic force microscopy (AFM). The present work is directed towards understanding the correlation of SAM molecular order and friction.

III. EXPERIMENT

A. Materials and methods

Self-assembled monolayers on Si (100) substrates were prepared using pentyltrichlorosilane (C$_5$ or C5), n-decyltrichlorosilane (C$_{10}$ or C10), dodecyltrichlorosilane (C$_{12}$ or C12), hexadecyltrichlorosilane (C$_{16}$ or C16), n-octadecyltrichlorosilane (C$_{18}$ or C18), and triacontyltrichlorosilane (C$_{30}$ or C30) purchased from Gelest and hexadecane (C$_{16}$H$_{34}$), chloroform (CHCl$_3$), and isopropyl alcohol (C$_3$H$_7$OH) purchased from Aldrich. The silicon (100) wafers were first cleaned using a microsurfactant followed by ethanol and then dried under a stream of nitrogen gas. These wafers were then treated using a plasma cleaner for 2 min to increase the OH$^-$ concentration at the top surface.

The SAMs were formed on the clean Si (100) substrates by first immersing them into solutions of 1 mM alkyltrichlorosilanes dissolved in hexadecane. The samples were left in the solutions for 24 h, after which they were removed and sonicated in CHCl$_3$, C$_3$H$_7$OH, and de-ionized water for 15 min, sequentially. Finally, the samples were annealed in an oven for 10 min at 125 °C. The advancing water contact angle measured (with an error of ±1.5°) for the C5 SAMs was 93.19°, C10 was 96.49°, C12 was 95.14°, C16 at 100.23°, 95.43° for C18 SAMs, and 101.38° for C30 SAMs indicates near-monolayer film coverage in all these cases.

B. NEXAFS experiment

NEXAFS at the carbon K edge was carried out at the National Synchrotron Light Source U7A NIST beamline. The incident soft x-rays are linearly polarized and monochromatic with an energy resolution of 0.2 eV at 300 eV. Multiple samples approximately $1 \times 1$ cm$^2$ on the Si wafer were freshly prepared with SAMs of different chain lengths and were loaded on a stainless-steel bar and introduced into the vacuum chamber through a sample load-lock system. Samples were precisely aligned with the aid of a fully automated computerized sample manipulator state. Energy resolution and photon energy calibration of the monochromator were performed by comparing gas-phase carbon monoxide with electron energy loss reference data. The partial-electron-yield (PEY) NEXAFS measurements at carbon K edge from 270 to 330 eV were obtained with a Channeltron at a negative 150 V bias on the entrance grid to enhance surface sensitivity (probe depth of approximately 3–5 nm). Under these bias conditions, the partial-electron-yield measurement is dominated by the Auger yield from the sample.

The sample was charge neutralized using a low energy electron flood gun, which added no noticeable background to the NEXAFS spectrum. Electron-yield data are subject to incident beam intensity fluctuations and monochromator absorption features. The spectra are normalized to the incident beam intensity $I_0$ by collecting the total electron-yield intensity from a clean gold-coated 90% transmitting grid placed in the incoming x-ray beam path.

IV. RESULTS AND DISCUSSION

Nanofrictional measurement was performed using an atomic force microscope (AFM) with a sharp tip. Figure 1 shows the coefficient of friction plotted in the right $Y$ axis as a function of carbon chain length and quantified molecular orientation distribution of SAMs measured by NEXAFS on the left $Y$ axis. It was observed that bare silicon has at least six times higher coefficient of friction compared to the trichlorosilane monolayer SAM system on Si. It is also ob-
served that C12 film exhibits the lowest coefficient of friction followed by C10, C5, C16, C18, and C30. The observed optimum friction value is contrary to the established observations of longer chain lengths that have lower friction values.\textsuperscript{7,19} In order to understand the differences better, these films were characterized by FTIR and NEXAFS. This article focuses on the use of NEXAFS to measure the molecular orientation and the degree of order in the film organization to enhance the understanding of the frictional measurements.

For each sample, the NEXAFS spectrum at carbon K edge was obtained at various angles \( \theta \) ranging from \( 20^\circ \) (glancing incidence) to \( 90^\circ \) (normal incidence), where \( \theta \) is measured between sample normal and polarization vector \( E \) of incident x-ray beam. Figure 2 shows NEXAFS PEY spectra for a C5 trichlorosilane SAM, C12 trichlorosilane SAM, and C30 trichlorosilane SAM at normal incidence when \( \theta = 90^\circ \) (solid curve) and at glancing incidence when \( \theta = 20^\circ \) (dashed curve) between \( E \) and surface normal.

Figure 2. NEXAFS carbon K-edge partial-electron-yield spectra for a C5 trichlorosilane SAM, C12 trichlorosilane SAM, and C30 trichlorosilane SAM at normal incidence when \( \theta = 90^\circ \) (solid curve) and at glancing incidence when \( \theta = 20^\circ \) (dashed curve) between \( E \) and surface normal.
SAMs. It has been shown by Genzer et al.\textsuperscript{26} that grafting densities vary significantly in semifluorinated mono-, di-, and trichlorosilane SAMs on Si. They also observed that the difference in grafting densities resulted in significantly different molecular order as estimated via NEXAFS. It is well known that the packing within SAMs is caused by a complex interaction of the chemical nature of SAMs and their bonding to the substrate, which influences their molecular organization.\textsuperscript{27} The differences in substrate and dialkylammonium binding sites may explain some of the differences observed between the work of Hähner et al. and the present study.

It is well known that conformation-sensitive regions in the infrared (IR) spectrum can be utilized to qualitatively measure the molecular order in the micron range in self-assembled monolayers.\textsuperscript{28} The frequency shifts in IR asymmetric CH\textsubscript{2} and symmetric CH\textsubscript{2} stretches illustrate the changes in conformational order in SAMs by comparing the frequency shifts to the reference. We employed complimentary FTIR spectroscopy on the n-trichlorosilane SAM system to check trends in order qualitatively and to compare with the NEXAFS results. Figure 4 shows the FTIR spectra in the reflection mode of trichlorosilane SAMs on silicon. These SAMs were prepared in the same way as for the NEXAFS studies. The asymmetric CH\textsubscript{2} band maxima is observed in the range of 2927–2912 cm\textsuperscript{-1}. Symmetric CH\textsubscript{2} stretches observed at 2853–2846 cm\textsuperscript{-1} are also indicated for various SAMs.

![Figure 3](image3.png)\textsuperscript{1487}

**FIG. 3.** Normalized PEY NEXAFS peak intensities vs sin\(^2\)(\(\theta\)) for (a) C5, (b) C12, and (c) C30 SAMs. The open circles represent C–C \(\sigma^*\) intensity and the filled squares represent the C–H \(\sigma^*\) intensity. Dichroic ratios indicated as \(R\) are calculated NEXAFS intensity at 90\(^\circ\) and interpolated NEXAFS intensity at 0\(^\circ\).

**TABLE I.** Dichroic ratio at C–H \(\sigma^*\) resonance measured via NEXAFS and coefficient of friction at load of 10 nN through AFM for trichlorosilane SAMs.

<table>
<thead>
<tr>
<th>SAM</th>
<th>Dichroic ratio</th>
<th>Coefficient of friction</th>
</tr>
</thead>
<tbody>
<tr>
<td>C5</td>
<td>0.065±0.03</td>
<td>0.09</td>
</tr>
<tr>
<td>C10</td>
<td>0.206±0.05</td>
<td>0.06</td>
</tr>
<tr>
<td>C12</td>
<td>0.283±0.02</td>
<td>0.03</td>
</tr>
<tr>
<td>C16</td>
<td>0.243±0.03</td>
<td>0.10</td>
</tr>
<tr>
<td>C18</td>
<td>0.223±0.03</td>
<td>0.11</td>
</tr>
<tr>
<td>C30</td>
<td>0.063±0.03</td>
<td>0.28</td>
</tr>
<tr>
<td>Bare Si</td>
<td>0.002±0.003</td>
<td>0.85</td>
</tr>
</tbody>
</table>

![Figure 4](image4.png)

**Fig. 4.** FTIR spectra in reflection mode of trichlorosilane SAMs with carbon chain lengths C5–C30 on silicon. The asymmetric CH\textsubscript{2} band maxima is observed in the range of 2927–2912 cm\textsuperscript{-1}. Symmetric CH\textsubscript{2} stretches observed at 2853–2846 cm\textsuperscript{-1} are also indicated for various SAMs.
measurement by Srinivasan et al. on titania substrate. FTIR measurements can be seen to complement the NEXAFS which has unequivocally proved to be extremely sensitive and effective in estimating molecular order.

From these observations, we can then interpret the friction data shown in Fig. 1. It appears that the optimum value of coefficient of friction is primarily caused by the film organization order and molecular chain alignment. A similar trend in frictional measurements was observed by Lio et al. on alkanethiols on gold and alkylsilanes on silica. Also plotted which has unequivocally proved to be extremely sensitive measurements can be seen to complement the NEXAFS resonance from NEXAFS measurements for the Cn SAMs. Table I summarizes the dichroic ratio from NEXAFS and coefficient of friction measurement from AFM and compares with bare silicon. A remarkable correlation in trends of the order from NEXAFS and coefficient of friction from AFM measurements is observed. SAMs with high dichroic ratio or most order have lower coefficient of friction. Combining the measurements from NEXAFS, FTIR, and AFM, nanofrictional coefficient measurement C12 SAMs emerges as the most ordered system possessing the least amount of friction, also supported by molecular dynamics simulations. Mikulski et al. examined the tribological behavior of n-alkane monolayer system by molecular dynamics simulation. Their studies revealed that in pure and highly ordered monolayers, resist pushing forces by a carbon tip and hence this resistance render a lower net friction in comparison to mixed alkane monolayers, which are relatively a more disordered system. These results taken together illustrate that molecular organization is an important factor for controlling frictional properties and may be the deciding factor in choosing the most suitable material for coating silicon devices for nanoscale lubrication.

V. CONCLUSIONS

n-alkyltrichlorosilane self-assembled monolayer films with different chain lengths (Cn films where n=5–30) were characterized by NEXAFS, FTIR, and AFM to understand the relationship of molecular organization and frictional characteristics. NEXAFS results concluded that alkylsilane chains with 12–18 carbon atoms formed an extremely ordered system. C12 SAMs had the highest molecular order and also had the least friction coefficient, as measured via AFM. Self-assembled monolayers of C5 and C30 were disordered. The C10 SAM system was partially ordered. FTIR spectroscopic measurement revealed similar order trends with the more quantitative NEXAFS technique. This study has unequivocally concluded that the molecular organization (which is critically dependent on chain length) is an important factor for controlling and predicting frictional properties. The information afforded from these complementary techniques has provided a unique opportunity to interpret the frictional properties of the monolayer films in relation to the molecular assembly and chain lengths.

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