

## Nano-scale Friction Properties of SAMs with Different Chain Length and End Groups

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**Abstract:** Friction characteristics at nano-scale of self-assembled monolayers (SAMs) having different chain lengths and end groups were experimentally studied. In order to understand the effect of the chain length and end group on the nano-scale friction: (1) two different SAMs of shorter chain lengths with different end groups such as methyl and phenyl groups, and (2) four different kinds of SAMs having long chain lengths (C10) with end groups of fluorine and hydrogen were coated on silicon wafer (100) by dipping method and Chemical Vapour Deposition (CVD) technique. Their nano-scale friction was measured using an Atomic Force Microscopy (AFM) in the range of 0-40 nN normal loads. Measurements were conducted at the scanning speed of 2  $\mu\text{m/s}$  for the scan size of 1  $\mu\text{m} \times 1 \mu\text{m}$  using a contact mode type  $\text{Si}_3\text{N}_4$  tip (NPS 20) that had a nominal spring constant 0.58 N/m. All experiments were conducted at ambient temperature ( $24 \pm 1^\circ\text{C}$ ) and relative humidity ( $45 \pm 5\%$ ). Results showed that the friction force increased with applied normal load for all samples, and that the silicon wafer exhibited highest friction when compared to SAMs. While friction was affected by the inherent adhesion in silicon wafer, it was influenced by the chain length and end group in the SAMs. It was observed that the nano-friction decreased with the chain length in SAMs. In the case of monolayers with shorter length, the one with the phenyl group exhibited higher friction owing to the presence of benzene rings that are stiffer in nature. In the case of SAMs with longer chain length, those with fluorine showed friction values relatively higher than those of hydrogen. The increase in friction due to the presence of fluorine group has been discussed with respect to the size of the fluorine atom.

**Key words:** nano, friction, SAM, tribology, AFM

### Introduction

Self-assembled monolayers, popularly known as 'SAMs' are molecular assemblies that form spontaneously by adsorption to substrates via high affinity chemisorption [1]. In the last decade these molecular assemblies have found their role as solid lubricants in MEMs tribology [2]. In MEMs devices, the surface area to volume ratio is large due to the scaling law [2]. Moreover, due to lateral and vertical gaps (clearances) between components being around 1  $\mu\text{m}$  [2], conventional liquid lubricants cannot be used, as they cause liquid-mediated adhesion leading to high static friction [3]. Further, during sliding, frictional effects not only due to external load but also due to the intrinsic liquid-mediated adhesive force needs to be overcome. Under such conditions, SAMs provide an ideal solution for lubrication [2,3] owing to their properties such as thermodynamic stability, formation of close packed structures, hydrophobicity and strong bonding (chemisorption) to the substrates [2,3].

For SAMs to be ideal candidates in tribology - to mitigate friction and wear, (i) the head group should be a polar group, for it provides strong adherence to the substrate through a chemical bond and (ii) the terminal group (end group) of the organic molecular chain should be a non-polar group [2]. An in

depth overview on various end and head groups, and classes of SAMs can be found in Ulmann's report [1]. Roya Maboudhian *et al.* [2] and Komvopoulos [4] provide insightful reviews on the tribological challenges in MEMs with the main focus on the evaluation of SAMs as lubricants. SAMs can be produced by various methods such as dipping, microcontact printing, sol gel, spin coating and by chemical vapor deposition [1,3-5].

In the present work, in order to understand the effect of the chain length and end group on the nano-scale friction of SAMs the following samples were tested: (1) two different SAMs of shorter chain lengths with different end group such as methyl and phenyl groups, and (2) four different kinds of SAMs having long chain lengths (C10) with end groups of fluorine and hydrogen. These SAMs were coated on Si-wafer by dipping and chemical vapor deposition (CVD) methods. In this article, the underlying mechanisms that influence the friction in these SAMs at nano-scale have been reported.

### Experimental

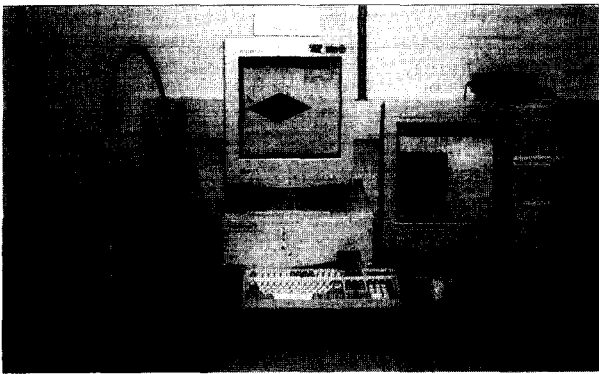
#### Test specimens

Table 1 shows the preparation method and water contact angles of SAMs. The di-phenyldichlorosilane (DPDC) and dimethyl-dichlorosilane (DMDC) have short chain lengths when compared to the rest of the SAMs. The decyltrichlorosilane (DTS) and perfluorodecyltrichlorosilane (FDTS) have 10 atoms of carbon

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**Table 1. Preparation method and water contact angles of SAMs**

Materials	Coating method	Water contact angle (Deg)
Si-Wafer	-	22
DPDC	CVD	84
DMDC	CVD	103
DTS	Dip	110
FDTS	Dip	112
DTMS	CVD	110
FDTMS	CVD	112

**Fig. 1. A view of AFM used for the measurement of nano-friction.**

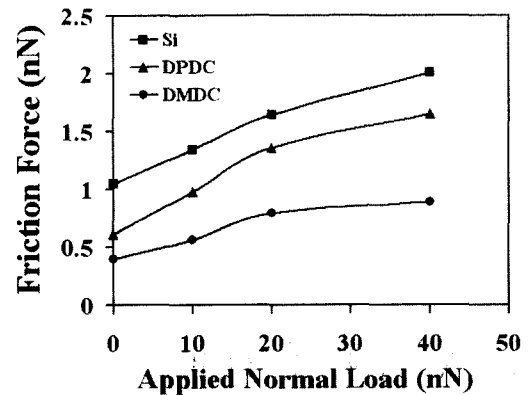
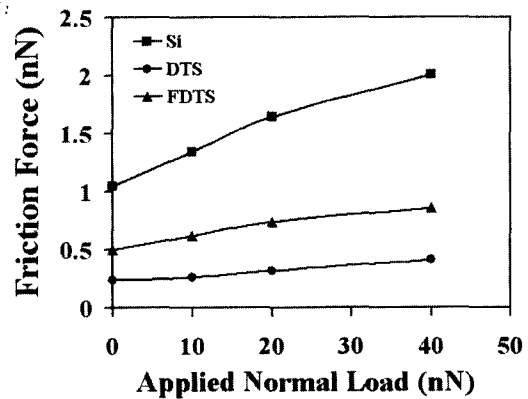
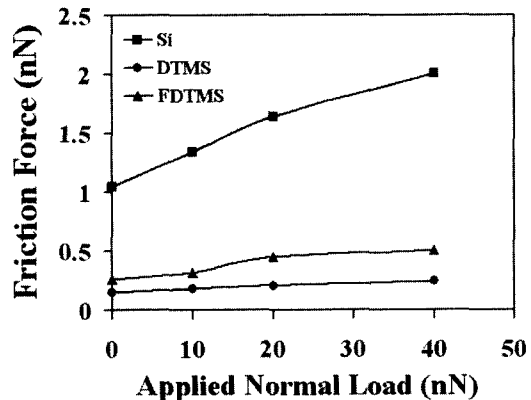
in their chain. The decyltrimethoxysilane (DTMS) and perfluorodecyltrimethoxysilane (FDTMS) also have 10 atoms of carbon in their chain. The difference between these two sets of long chain SAMs is that DTS and FDTS were prepared using the dip method, whereas DTMS and FDTMS were prepared using the CVD technique.

### Test apparatus

The nano-scale friction of SAMs was measured using an Atomic Force Microscopy (AFM) in the range of 0-40 nN normal loads, in LFM (Lateral Force Microscope) mode. Figure 1 shows a view of the AFM used in the present work. Measurements were conducted at the scanning speed of  $2 \mu\text{m/s}$  for the scan size of  $1 \mu\text{m} \times 1 \mu\text{m}$  using a contact mode type  $\text{Si}_3\text{N}_4$  tip (NPS 20) that had a nominal spring constant  $0.58 \text{ N/m}$ . All experiments were conducted under controlled temperature ( $24 \pm 1^\circ\text{C}$ ) and relative humidity ( $45 \pm 5\%$ ).

### Results and Discussion

Figures 2 and 3 show the variation of nano-scale friction as a function of applied normal load in SAMs with short chain lengths (DPDC, DMDC) and long chain SAMs (DTS, FDTS) respectively. Figure 4 shows the nano-friction of long chain SAMs DTMS and FDTMS. The friction values of Si-wafer are also shown in these graphs. All SAMs exhibit superior frictional behaviour than Si-wafer. From these figures it is worth noting that the friction force exists even at the zero applied normal load. This is mainly attributed to the bonding

**Fig. 2. Nano-friction of Si-wafer and short chain SAMs (DPDC and DMDC).****Fig. 3. Nano-friction of Si-wafer and long chain SAMs (DTS and FDTS).****Fig. 4. Nano-friction of Si-wafer and long chain SAMs (DTMS and FDTMS).**

under different circumstances [2]. In Si-wafer, owing to its hydrophilic nature (Table 1) it is considered that the capillary force due to the formation of meniscus-bridge (condensation of water from the environment) between the tip and the sample, contributes to a major extent. Van der Waal forces also contribute [6], but their magnitude is less when compared to that of the capillary force [2]. In contrast to Si-wafer, SAMs are hydrophobic in nature (Table 1) and hence, capillary force gets suppressed to a large extent. Further, friction in nano-scale

is in a regime where the contribution from intrinsic adhesion can outweigh those from the asperity deformation and ploughing [2,7]. In the present case, the applied normal load has been limited to 40 nN, in an effort not to deform or wear the SAMs, but rather to probe the frictional properties of only the outermost portions of the SAMs. Under the condition that the friction in the present case has not been influenced by the deformation, the intrinsic adhesion contributes strongly to the friction force [2,7], thus rendering the Si-wafer to have higher friction force than the SAMs. Further, SAMs exhibit lower friction force than the Si-wafer owing to their smaller real area of contact due to their lower interfacial energy, which is indicated by their higher water contact angles (Table1) [8]. In addition to lower contact area, another important feature that reduces friction in SAM is its molecular chains. These chains exhibit significant freedom of swing and thereby rearrange along the sliding direction under shear stress, which eventually yields a smaller resistance during sliding, thereby exhibiting lower friction [9].

It could be observed from the Figs. 2, 3 and 4, that the friction force decreases as a function of chain length. SAMs with C10 show friction values lesser than the short chain SAMs (DPDC, DMDC). This is due to the reason that the monolayers with longer chains are more ordered and are more densely packed in comparison to those with shorter chain lengths [3]. It has been reported earlier by Camillone *et al.* [10] that there exists a direct relation between the chain length and the packing density. Thus, it seems that in the case of longer chain SAMs the packing density of the chains increases, which in turn increases the order within the monolayer that eventually decreases friction. The effect of packing density on the friction behaviour of SAMs has also been reported by McDermott *et al.* [11]. In their work, they studied the effect of alkyl chain length on the frictional properties of SAMs using AFM. They reported that the longer chain monolayers exhibited a markedly lower friction than shorter chain monolayers. They conducted infrared reflection spectroscopy to measure the bandwidth of the methylene stretching mode, which exhibits a qualitative correlation with the packing density of the chains. It was found that monolayers with longer chains are more ordered and more densely packed in comparison to those with shorter chain lengths. They further reported that the long chain monolayers retain molecular scale order during shear, resulting in lower friction values. Xiao *et al.* [12] and Lio *et al.* [13] also studied the effect of the length of the alkyl chain on the friction properties of SAMs. They too observed that longer chain SAMs exhibited superior friction property than short chain SAMs. Further, they suggested that longer chains stabilized by van der Waals attraction, form more compact and rigid layers and act as better lubricants. Molecular dynamics simulations also have shown that long chain lengths SAMs exhibit better frictional properties than their short length counterparts [14]. In comparison to long chain SAMs, the short chain SAMs are less ordered and have large number of dissipative modes that leads to much higher friction forces [3].

It could also be observed from Figs. 3 and 4 that the long chain SAMs namely DTMS and FDTMS show friction values

less than DTS and FDTS. This is because of the difference in their coating method. In the case of DTS and FDTS, particles (agglomerates) were observed at the surface, which were because of polymerization during the dip coating process. The presence of these agglomerates would increase the friction in the case of DTS and FDTS. In DTMS and FDTMS, the agglomerate formation was absent because of the coating technique namely the CVD method [8]. This explains for the lower friction values in DTMS and FDTMS.

In the present work, amongst the short chain SAMs (DPDC, DMDC), the DPDC SAM shows higher friction values. This could be understood by considering the “molecular spring model” proposed by Bhushan *et al.* [15]. According to this model, an AFM tip sliding on the surface of SAM is like a tip sliding on the top of “molecular springs or brush”. Such a molecular spring assembly has compliant features and can experience orientation and compression under normal load. The orientation of the “molecular springs and brush” under normal load reduces the shearing force at the interface, which in turn reduces the friction force. The possibility of the orientation is determined by the spring constant (stiffness) of a single molecular chain, as well as the interaction between the neighboring molecules, which can be reflected by packing density or packing energy [15]. Thus, it is important to note that not only does the packing density influences the friction behaviour, but the stiffness of the molecular chain too plays an important role. In the present case, the increased friction force exhibited by DPDC is mainly because of the higher stiffness that is affected by the benzene ring when compared to that of the linear chain in DMDC. The higher stiffness in DPDC is brought forth by the basic nature of the benzene ring, which is due to the saturated bonds (double bonds) [15].

In the SAMs with the long chain lengths namely C10 (Fig. 3, 4), FDTS and FDTMS show friction values relatively higher than those of hydrogen terminated ones (DTS, DTMS). This could be attributed to the presence of fluorine atom in their chemical structure. Fluorine atoms have larger Van der Waals radii [16,17]. Consequently, they interact more strongly with the neighboring chains, giving rise to long-range multi-molecular interactions. To overcome the energetic barrier due to the long-range multi-molecular interactions, more energy gets imparted to the molecular film during sliding and results in higher frictional property. Further, the fluorinated films experience additional energetic barriers to rotation about the chain axis [12,16].

Furthermore, there exists a possibility of the formation of point defects (vacancies) within these fluorinated films due to the relatively large size of the fluorine terminal group [16]. It could also be possible that these defects which although remain invisible to the imaging process [18], could give rise to additional energy dissipation and thereby increase the friction.

Interestingly, Kim *et al.* [17] have demonstrated that the introduction of large size atom like fluorine reduces monolayer order and increases friction. As an example they introduced small percentages of  $CF_3$  termini into  $CH_3$ -terminated SAMs and observed that it led to a substantial increase in the frictional response of the monolayer. They suggested that the

magnitudes of the frictional response correlate directly with the size of the terminal groups in SAMs.

### Conclusions

In this work we evaluated the nano-scale frictional behaviour of SAMs with different chain lengths and end groups. The following are the conclusions drawn from the present work:

(1) At nano-scale, SAMs exhibit superior frictional property than Si-wafer owing to their lower inherent adhesion and smaller contact area affected by their lower interfacial energies.

(2) The nano-friction in SAMs was affected by their chain length and also by their end terminal groups.

(3) Long chain SAMs exhibited superior friction than short chain SAMs due to their higher packing energy.

(4) Phenyl terminated SAMs exhibit increased friction due to increased stiffness induced by the benzene rings.

(5) Fluorine termination increases friction, which is due to the effect of the larger Van der Waals radii of the fluorine atom.

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