Tribology of PFPE overcoated self-assembled monolayers deposited on Si surface

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Abstract
Friction and wear characteristics of monomolecular layers of self-assembled monolayers (SAMs) with and without perfluoropolyether (PFPE) overcoat were studied using ball-on-disk experiments. Ultra-thin layer of PFPE was dip-coated onto two different SAMs, one with non-reactive terminal group (octadecyltrichlorosilane (OTS)) and the other with reactive terminal group (3-aminopropyltrimethoxysilane (APTMS)), which were formed on Si substrate by self-assembly. The effects of PFPE overcoating on physical and chemical properties were evaluated using contact angle measurement and x-ray photoelectron spectroscopy. For a comparison, PFPE was also coated onto the Si surface and their properties were evaluated. All PFPE modified surfaces were baked at 150°C for 2 h, to investigate the effect of thermal treatment on tribological properties. PFPE coating has shown higher water contact angles irrespective of the SAM surface. Coating of PFPE on both SAM surfaces has lowered their coefficients of friction. PFPE overcoating has shown remarkable increase in the wear resistance when it was coated on reactive APTMS SAM and little increase on OTS SAM. Thermal treatment after PFPE coating onto SAMs further reduced the coefficient of friction to a smaller extent. Moreover, thermal treatment has shown an additional increase in wear-life by approximately 30% in the case of PFPE coated APTMS SAM surface and a decrease in the wear-life in the case of PFPE coated OTS SAM. The reasons for these observed phenomena are explained in terms of the amounts of PFPE bonded or mobile, surface energies of SAMs, uniformity and molecular packing of SAM surfaces.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Micro-miniaturization is a current trend in the development of electromechanical devices known as microelectromechanical systems (MEMS) [1]. MEMS have been receiving much attention because of their potential applications in areas such as mechatronics, biomedical communications and chemical technology [2, 3]. The performance of MEMS components is limited because of their large surface area-to-volume ratios. The electrostatic and other surface forces, in this case, become predominant with reference to inertial and gravitational forces. Hence contact related adhesion and friction phenomena become stringent problems [4]. Because of the micron size of the MEMS components, conventional oil-based lubricants are not desirable as the viscous forces can be quite large in comparison to the driving forces involved in running those components [5]. Currently Si is the most popular material for MEMS components. Si demonstrates very poor tribological

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properties and hence realization of the true potential of MEMS may not be possible without the improvement in tribology of Si surfaces.

Ultra-thin organic molecular layers have been proposed as the lubricants for Si based MEMS systems [2, 5, 6]. The lubricant layers, generally, can be formed by two methods: (1) the Langmuir–Blodgett method, and (2) the self-assembly method [7]. The first method cannot be used for three-dimensional surfaces and is mainly concerned with flat surfaces such as magnetic recording media [8–11] and moreover, these L–B films are only physically bonded with the substrate by van der Waals forces which are weaker in comparison to chemical bonds [12]. Much attention has been paid recently to self-assembled monolayers (SAMs) because of easy preparation and their excellent properties such as low thickness, stable chemical and physical properties and good covalent bonding with the substrate. Moreover, the properties of the SAMs can be widely varied by changing the type and length of the molecules, terminal group and the degree of cross linking within the layer, which makes them more attractive than the L–B films [7].

Alkyl silane SAMs have been extensively studied and proposed as the lubricants for MEMS [8, 13–15]. They can reduce coefficient of friction, stiction and wear when they are deposited onto the Si substrate [4, 16, 17]. However, despite low coefficient of friction, the wear resistance achieved by these monomolecular layers is not sufficient to provide long life to the high velocity moving MEMS components [18]. These monolayers do not demonstrate high wear durability either because there is no mobile portion of the lubricant or because of some molecular properties which are not well understood. Once wear initiates the molecules are easily removed from the contact area and there is no replenishment in these layers. The worn particles often also act as a third body and thus accelerate the wear of the film. Therefore, researchers have realized the importance of the mobile portion as the top layer which will give self-repairability due to the migration of mobile molecules into the sliding contact, leading to high wear resistance [19]. This concept has been well studied for hard disk lubrication. For hard disk lubrication, a combination of both bonded and mobile perfluoropolyether (PFPE) has shown higher durability than only either bonded or mobile PFPE [20–22]. Recent studies by Choi *et al* [23] revealed that the PFPE-coated SAMs, which were deposited onto hydrogenated amorphous carbon surfaces, show higher durability than only SAM coated or PFPE coated carbon surfaces. Recent studies of MEMS lubrication utilized the concept of using both bonded and mobile portions of PFPE which have shown good improvement as far as wear durability is concerned [24]. The concept of utilizing the mobile PFPE to enhance wear durability of SAMs with different functional groups or polymer films has not been tried in view of MEMS lubrication. Julthongpiput [25] proposed this concept of PFPE overcoating to enhance the wear resistance of epoxy nanocomposite bilayers, however, the results are not available.

In this study, we have focused on the effect of coating PFPE onto a single monolayer of SAMs with two different terminal groups: one hydrophilic 3-amin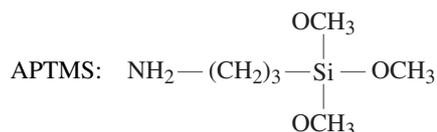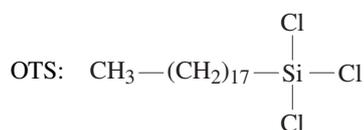opropyltrimethoxysilane (APTMS) and the other hydrophobic octadecyltrichlorosilane (OTS). PFPE is selected as the top layer because of its properties such as low surface tension, chemical and thermal stability, low vapour pressure, high adhesion to the substrate and good lubricity [26]. The aim is mainly to investigate the effects of the PFPE overcoating (mobile and partially bonded) on the wear lives of SAM layers. PFPE was coated onto the two SAMs which had polar/non-polar terminal groups. They were then subjected to strong shearing conditions in contact sliding to evaluate the wear characteristics. Their tribological properties were finally compared with bare Si and SAM coated surfaces without PFPE overcoat.

Much of the study on ultra-thin film lubrication has been carried out in the past using atomic force microscope (AFM) with the lateral force measurement option. Despite very accurate measurement of the coefficient of friction by AFM this instrument does not represent actual surface contacts of a microsystem such as MEMS. Firstly, this is because the AFM tip is a point contact whereas in MEMS components the surface areas in contact are much larger. Secondly, the sliding speed achievable in AFM is extremely low in comparison to the speeds required for microsystems. Therefore, in our study we have used a ball-on-disk type tribometer which has realistic sliding contact area (with track width in the range of a few hundred microns) and where the sliding velocity is high. Because of the larger contact area and higher sliding speed we believe that the results of this study may be applicable to a range of microsystems where the contact area could be in the range of $100\,\mu$m. Moreover, the AFM test can be used only for a limited number of cycles of sliding, while for practical applications we often require wear-life data for 10^5–10^8 numbers of cycles which can be obtained easily in a rotating type of tribometer.
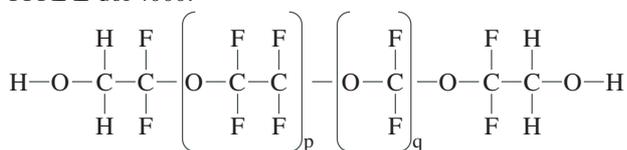
2. Experimental

2.1. Materials

Polished single crystal silicon (100) wafers were used as the substrate. These Si wafers were cut into pieces of approximately $2\,\text{cm} \times 2\,\text{cm}$ and then used for the surface modification. OTS and APTMS obtained from Aldrich Inc. were used for the preparation of SAM solution without further purification. OTS produces a non-polar methyl terminal group (CH_3) on the surface whereas APTMS generates the polar amine terminal groups (NH_2) after deposition. A commercial PFPE Zdol 4000 (molecular weight $4000\,\text{g mol}^{-1}$, monodispersed) was used to coat the SAM surfaces and bare Si. PFPE molecules have terminal OH groups at their ends. The chemical formulae of the two SAMs and PFPE used are as follows:

$$\text{OTS:} \quad CH_3 - (CH_2)_{17} - \underset{\underset{Cl}{|}}{\overset{\overset{Cl}{|}}{Si}} - Cl$$

$$\text{APTMS:} \quad NH_2 - (CH_2)_3 - \underset{\underset{OCH_3}{|}}{\overset{\overset{OCH_3}{|}}{Si}} - OCH_3$$

PFPE Z-dol 4000:

$$H-O-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-\underset{\underset{F}{|}}{\overset{\overset{F}{|}}{C}}-\left[O-\underset{\underset{F}{|}}{\overset{\overset{F}{|}}{C}}-\underset{\underset{F}{|}}{\overset{\overset{F}{|}}{C}}\right]_p-\left[O-\underset{\underset{F}{|}}{\overset{\overset{F}{|}}{C}}\right]_q-O-\underset{\underset{H}{|}}{\overset{\overset{F}{|}}{C}}-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-O-H$$

where the ratio p/q is 2/3. Hydrofluoropolyether solvent (H-Galden ZV) purchased from Ausimont Inc. was used for the preparation of PFPE solution without further purification. Toluene (99.5% anhydrous), methanol (99.8%) and distilled water were also used for the preparation of the SAMs.

2.2. Preparation of SAMs

Si substrate was ultrasonically cleaned with soap water and distilled water followed by rinsing with acetone for 10 min in order to get rid of organic contaminants. The samples were then hydroxylated by immersing in a piranha solution (a mixture of 7 : 3 (v/v) 98% H_2SO_4 and 30% H_2O_2) at 60°C to 70°C for 50 min. In addition to the hydroxylation, piranha treatment removes any organic/inorganic contaminants. The root-mean-square (rms) roughness of these wafers after piranha treatment was 0.3–0.5 nm which was measured using AFM. The wafers were then rinsed with distilled water and acetone in succession and dried by blowing N_2 gas. The cleaned substrates were subsequently immersed into the respective SAM solutions of OTS or APTMS with 5 mM or 3 mM concentrations, respectively, and were held for 5–6 h. The modified substrates were sequentially washed with toluene and methanol to remove any physisorbed impurities on SAM molecules and finally, the samples were dried with N_2 purge.

2.3. Dip-coating of PFPE onto SAM modified and unmodified Si substrates

PFPE was coated onto SAM modified Si substrates using a custom-built dip-coating machine. Prior to dip coating a solution of PFPE in H-Galden solvent was prepared. The concentration of PFPE in the solution was 0.2 wt%. The SAM modified Si substrates were dipped into the PFPE solution and held for 1 min and then withdrawn at a constant speed of 2.1 mm s^{-1}. Similarly, bare Si after piranha treatment was also coated with PFPE. All samples were stored in desiccator until use. Tribological tests were carried out almost immediately after PFPE coating without any delay to eliminate the ageing effect at room temperature. For the thermal treatment study, the PFPE coated samples were baked at 150°C for 2 h in vacuum.

Extensive rinsing has been carried out after PFPE coating and after annealing, with the same solvent used for dip-coating, to measure the atomic percentage of F (fluorine) remaining after rinsing (using x-ray photoelectron spectroscopy, XPS) which is then used to estimate the amount/percentage of PFPE bonded to the SAM or Si surfaces. Such rinsing removes only the mobile portion of PFPE whereas the bonded part remains firmly attached to the substrate.

2.4. Depositional characterization and surface analysis

The static contact angles for distilled water on the unmodified and modified surfaces were measured with VCA Optima

Contact Angle System (AST Products, Inc. USA). A water droplet of 0.5 to 1 μl was used for contact angle measurement. At least five to six replicate measurements, for three different samples, were carried out and an average value was taken. The variation in water contact values at various locations of a sample is within $\pm 2°$. The measurement error was within $\pm 1°$.

The surface morphology of SAM modified Si substrates was investigated using Dimension 3000 AFM (Digital Instruments, USA). All images were collected in air using the tapping mode and a monolithic silicon tip. The set point voltage used was 1–2 V and the scan rate was 1 Hz.

The chemical state of the sample surface, before and after PFPE coating, with and without thermal treatment and after extensive rinsing of PFPE was studied by XPS. Measurements were made on a Kratos Analytical AXIS HSi spectrometer with a monochromatized Al Kα x-ray source (1486.6 eV photons) at a constant dwell time of 100 ms and pass energy of 40 eV. The core-level signals were obtained at a photoelectron take-off angle of 90° (with respect to the sample surface). All binding energies (BE) were referenced to the C1s hydrocarbon peak at 284.6 eV.

2.5. Tribological characterization

Friction and wear tests were carried out on UMT-2 (Universal Micro Tribometer, CETR, USA) using ball-on-disk mode. A Si_3N_4 ball of 4 mm diameter was used as the counterface. The rotating speed of the spindle was 100 rpm giving a sliding speed of 0.021 ms^{-1} at a track diameter of 4 mm. The roughness of the ball used was 20 nm as provided by the supplier. The ball was cleaned ultrasonically with acetone before the test. Every ball was viewed under the optical microscope to ensure that it was free from contaminants or manufacturing defects. For each test a new ball was employed. The normal load used was 5 g, which gave a contact pressure of approximately 330 MPa (calculated using the Hertzian Contact Model). Although the typical contact pressures in MEMS are in the order of few megapascals (or less than 1 MPa) [27] we set the contact pressure at 330 MPa to shorten the duration of the wear tests. A lubricant which can perform well at high pressure is also expected to give satisfactory performance at low pressures. All experiments were performed in air at room temperature (23°C) and at a relative humidity of approximately 70%. In this paper the initial coefficient of friction was reported after 4 s of sliding (i.e. 6 cycles of disk rotation) after stabilization of the sliding process. The tribometer constantly measures normal load and friction force and gives the coefficient of friction as real-time ratio. The wear-life was defined as the number of cycles after which coefficient of friction exceeded a value of 0.3 or a visible wear scar appeared on the substrate, whichever happened earlier. This strategy was adopted to define the wear-life, because of the reason that in some tests, even when a clear visible wear track appeared, the coefficient of friction was less than 0.3. Our evaluation method of wear-life is consistent with the literature for similar kinds of tests [24, 28]. The wear-life data have been obtained on at least five different samples utilizing at least two different tracks on each sample and an average of the three best results is reported.
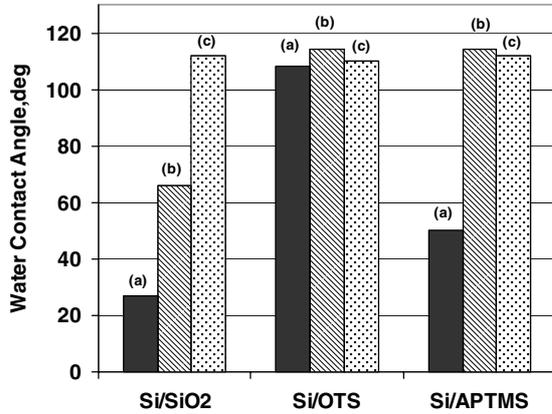
Figure 1. Water contact angles of bare Si, OTS SAM and APTMS SAM with and without PFPE overcoat and with thermal treatment after PFPE overcoating. (*a*) No PFPE overcoat, (*b*) PFPE overcoat and (*c*) PFPE overcoat followed by thermal treatment.

3. Results

3.1. Contact angle results

The water contact angles of bare Si, SAM surfaces with, and without, PFPE overcoat and thermally treated PFPE overcoat, are shown in figure 1. The water contact angles of OTS and APTMS SAM surfaces are 108° and 50°, respectively, while bare Si shows a contact angle of 27° which reveals the differences in their surface energies/wetting characteristics. The change in the water contact angles after OTS and APTMS deposition also reveals their successful formation. Coating of PFPE onto bare Si after piranha treatment changed the contact angle from 27° to 66°. This is in good agreement with the findings reported in the literature [29]. Irrespective of their surface energies PFPE coating on the two SAM surfaces has shown a contact angle of 114°. This reveals that, whatever the surface condition of SAM, PFPE coating lowers the surface energy. Even though the atomic concentration of F is the same when PFPE is coated onto APTMS SAM and bare Si (from the XPS results to be presented in the coming sections), the contact angle is less in case of PFPE coated Si (only 66°) than PFPE coated APTMS SAM (114°). The reasons for this difference in the contact angles for PFPE coated Si and SAM surfaces are presently not very clear. Low surface energy is one of the important properties that are required for MEMS components because surfaces with high energy lead to stiction and early failure. Therefore the low wettability/surface energy of these PFPE coated surfaces indicates that they can alleviate the problem of stiction arising from the capillary forces in the MEMS components [30, 31].

3.2. Morphology of SAM surfaces

AFM studies were carried out to observe the surface morphology of bare Si, OTS SAM and APTMS SAM surfaces and the results are shown in figure 2. Some small particles present on the bare Si could be from atmospheric contaminants which were difficult to get rid of. The rms roughness of bare Si was 0.41 nm measured over a 1 μm × 1 μm area. OTS SAM has shown a featureless and smooth surface. The rms roughness over 0.5 μm × 0.5 μm area for OTS was

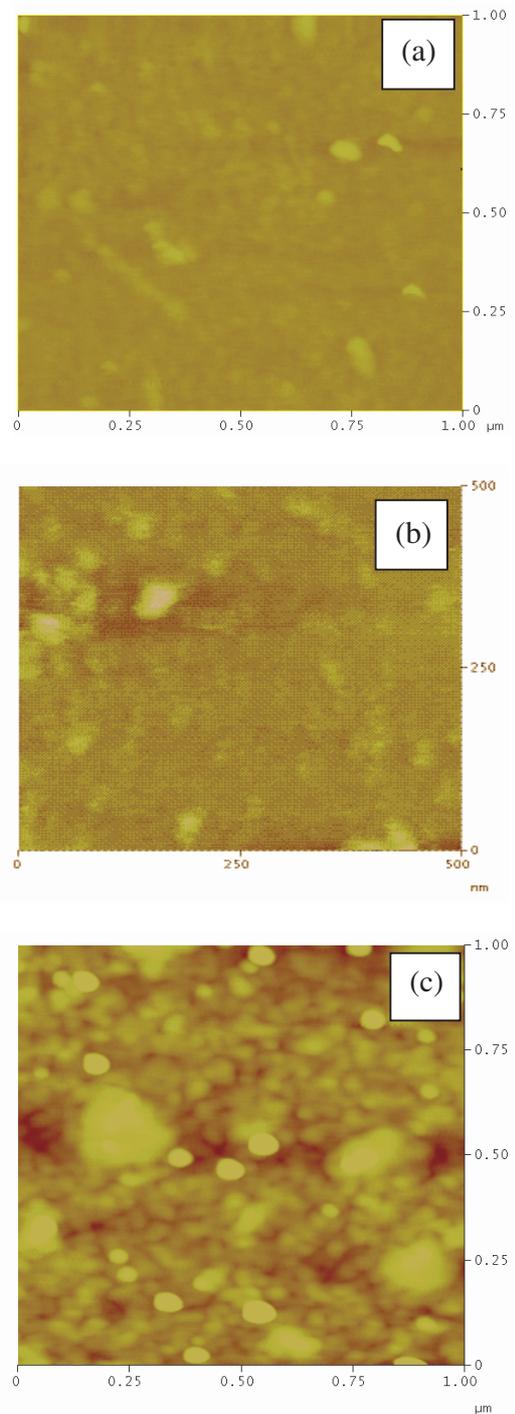**Figure 2.** AFM images of (*a*) bare Si, (*b*) OTS SAM and (*c*) APTMS SAM showing surface features in a scan area of 1 μm × 1 μm for (*a*) and (*c*); 500 nm × 500 nm for (*b*). Vertical scale is 10 nm. The rms roughness values are 0.41 nm, 0.25 nm and 1.7 nm for bare Si, OTS SAM and APTMS SAM, respectively. Note that the surface features shown in these images are of submicron scale.

0.25 nm. These results indicate that the SAM of OTS on the silicon wafer is quite smooth and homogeneous. APTMS SAM contains many islands which are distributed randomly on the surface. The average island size of APTMS SAM is large and is due to the bulk polymerization of APTMS molecules which in turn is due to the hydrogen bonding

between the APTMS molecules themselves and with surface hydroxyl groups, which has been studied extensively by Zhang and Srinivasan [32]. This leads to many pores/gaps between islands of APTMS molecules often exposing the substrate. The roughness value for APTMS is 1.7 nm, over $1\,\mu m \times 1\,\mu m$ which is higher than that of bare Si and OTS SAM. The difficulty in getting the uniform films of functional SAMs, such as APTMS, has been reported in the literature [33]. The change in the morphology after SAM deposition demonstrates the successful formation of SAMs.

3.3. XPS results

Figure 3 shows the wide scan spectrum of the XPS measurements for bare Si and two SAMs. Bare Si has shown
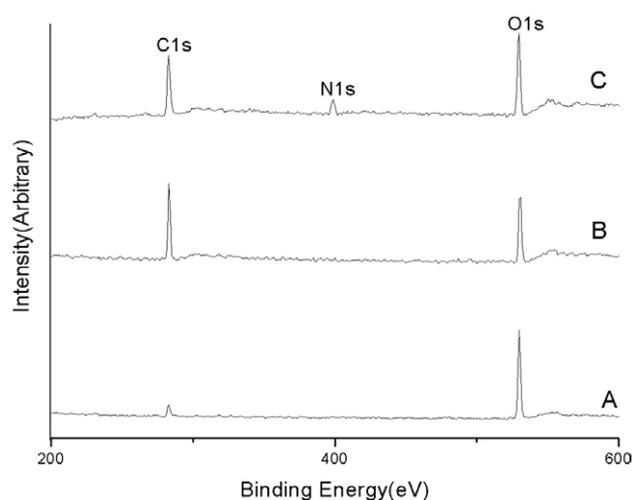
the largest O1s peak which is from its oxide. The presence of lesser intensity C1s peak on the bare Si might be due to the organic contaminants that were not removed during the piranha treatment or those adsorbed from the atmosphere during handling before XPS test [24]. OTS SAM has registered highest atomic concentration of C that is due to its longer chain length. APTMS SAM has shown the presence of N1s peak which is because of its amine terminal group on the surface. Finally, the wide scan spectrum shown in figure 3 confirms the successful formation of two SAMs on Si surface and the cleanliness of the bare Si surface.

Wide scan XPS spectra of PFPE coated surfaces and the atomic ratios of fluorine are shown in figure 4. Presence of F 1s peak on three PFPE coated surfaces supports the presence of the PFPE. The atomic per cent of F is less when PFPE was coated onto OTS SAM in comparison to the other two surfaces. It is 7.81% when PFPE is coated onto OTS SAM whereas it is 40.31% and 41.23% when PFPE is coated onto bare Si and APTMS SAM surfaces, respectively. This difference is mainly due to the hydrophobic nature of the OTS SAM surface because of which a lesser amount of PFPE can wet the surface during dip coating. We have measured the contact angles using H-Galden (the solvent used for PFPE) on SAM modified Si surfaces and bare Si to check the wetting characteristics of H-Galden and we found a value of approximately 14° on all surfaces which indicates that the solvent itself was able to wet all the surfaces. The lower amount of PFPE in case of OTS modified Si is only due to the low surface energy of the OTS rather that the fact that less PFPE was coated onto OTS during dip-coating due to solvent effect.

Figure 5 shows the atomic concentrations of F on the PFPE coated surfaces, PFPE coated followed by rinsed surfaces and thermally treated PFPE followed by rinsed surfaces, as obtained from XPS data. From these atomic percentages of F the amount of PFPE bonded is estimated. XPS results clearly
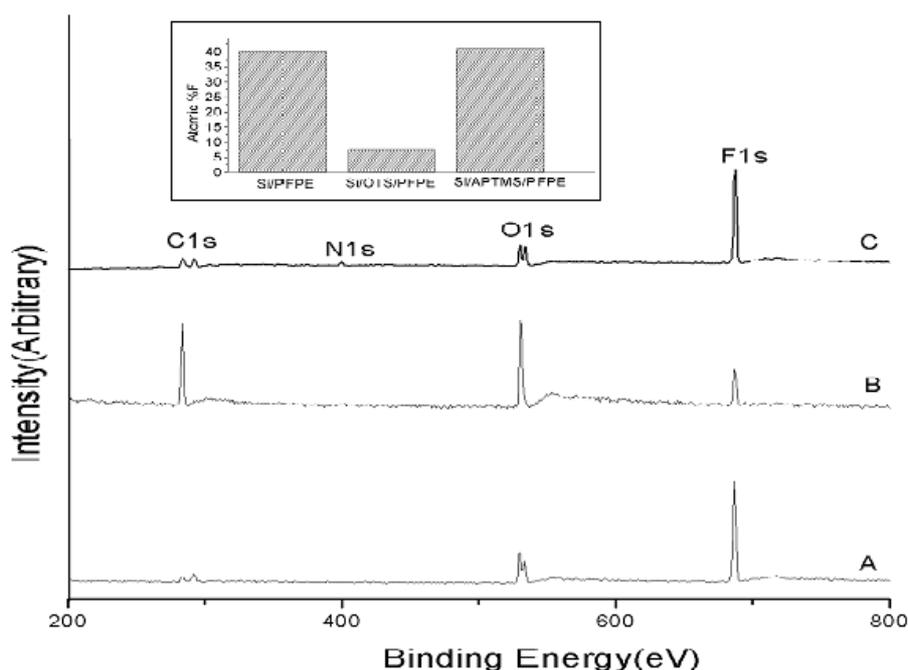

Figure 3. XPS wide spectrum for (A) bare Si, (B) Si/OTS and (C) Si/APTMS surfaces.

Figure 4. XPS wide spectrum for (A) Si/PFPE, (B) Si/OTS/PFPE and (C) Si/APTMS/PFPE. The inset shows the atomic concentrations of F determined from XPS on as-lubed PFPE on Si, OTS SAM and APTMS SAM surfaces.
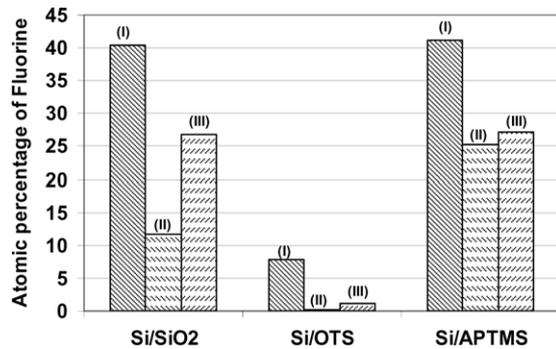
Figure 5. Atomic percentages of fluorine on PFPE coated bare Si, Si/OTS and Si/APTMS samples before and after rinsing and on thermally treated PFPE coated samples after rinsing. (I) PFPE-as lubed, (II) PFPE-lubed and rinsed and (III) PFPE-lubed, thermally treated and rinsed.

indicate that about 60% of PFPE remains on the APTMS SAM surface followed by about 30% on bare Si whereas a negligible (3%) amount of PFPE remains on OTS surfaces after rinsing.

The portion of PFPE remaining on the surface after rinsing with H-Galden on bare Si and APTMS modified Si are bonded through hydrogen (H)-bonding. Negligible amounts of PFPE remain on the OTS SAM after rinsing because there is no possibility of bonding between the methyl groups of OTS and alcohol groups of PFPE. The strongly adsorbed PFPE has implications on tribological properties, especially on wear resistance, which will be discussed in the later sections.

3.4. Tribological results

Figure 6 shows the coefficient of friction of bare Si, OTS SAM and APTMS SAM surfaces, with and without PFPE overcoat and thermally treated PFPE overcoating. OTS SAM has shown a coefficient of friction of 0.18 whereas bare Si and APTMS SAM without PFPE have shown values of 0.6 and 0.5, respectively. Among these three surfaces OTS SAM has the lowest coefficient of friction showing a remarkable decrease in the friction of the bare Si. Irrespective of the initial coefficient of friction of these surfaces PFPE coating has shown a coefficient of friction of about 0.15–0.20 for all three cases. Therefore, the initial coefficient of friction after PFPE coating is independent of the surface condition before coating. We found the ranking of the coefficient of friction in the order (high to low): bare Si > APTMS SAM > APTMS/PFPE > OTS SAM > Si/PFPE > Si/OTS/PFPE. Thermal treatment of the PFPE coated samples, in all cases, reduced the coefficient of friction to a lower value of about 0.13.

The wear-life, that is, the number of cycles after which the film fails, for bare Si, OTS SAM and APTMS SAM surfaces before and after PFPE coating and for thermally treated PFPE coated samples are shown in figure 7. In addition to the average values, error bars that contain the minimum and maximum wear-life values among three tests are also shown in figure 7 in order to highlight the scatter among the data. The large variation in some of the tests is due to the sensitivity of the thin-film lubrication to the experimental conditions. The variations of the wear-life cycles in this study, are comparable with the findings in the literature [28, 34, 35]. Without PFPE, both bare Si and APTMS SAM have shown higher initial
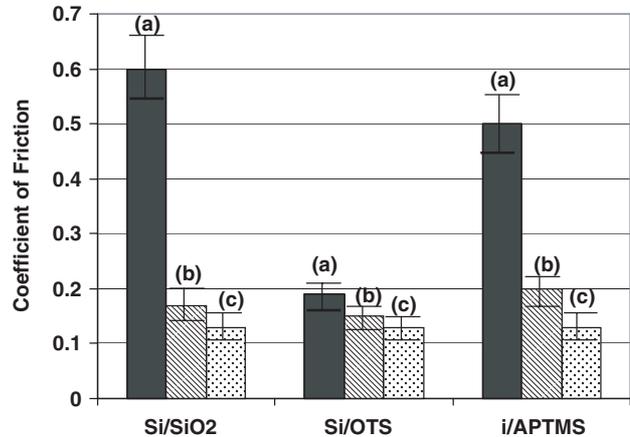

Figure 6. Coefficient of friction when sliding a 4 mm diameter silicon nitride ball against bare Si, OTS SAM and APTMS SAM with and without PFPE overcoat and after thermal treatment of the PFPE coating. (a) No PFPE overcoat, (b) PFPE overcoat and (c) PFPE overcoat followed by thermal treatment. The measurement of the coefficient of friction was taken 4 s after the start of the test. The plotted data are average values of three runs for each case. Data scatter bars are presented in the graph.

coefficient of friction and failed within few tens of cycles of sliding. A clear visible wear track appeared very early during the sliding process. OTS SAM has shown a wear-life of ∼1600 cycles. Details of tribological properties of these three surfaces are reported in [36]. As a whole, PFPE coating has increased the wear-life of all three different surfaces. There is a remarkable increase in the wear-life when PFPE is coated onto the bare Si and APTMS SAM surfaces, but negligible improvement is noticed when it is coated onto OTS SAM. PFPE coating onto the bare Si has shown a wear-life of ∼5000 cycles. Even though the APTMS SAM alone did not show good tribological properties, PFPE coating increased the wear-life to an extent of 5200 cycles. PFPE coating onto the OTS SAM has resulted in an increase in the wear-life from 1600 to 2500 cycles. In all the three cases PFPE coating helped in improving the tribological properties (both friction and wear). The increase in wear-life is more in the case of PFPE coated APTMS SAM when compared to PFPE coated OTS SAM even though OTS SAM exhibits higher wear-life than that for APTMS SAM without PFPE. The ranking of the wear durability of these surfaces from most wear durable to the least is as follows: Si/APTMS/PFPE > Si/PFPE > Si/OTS/PFPE > OTS SAM > APTMS SAM or bare Si.

Thermal treatment has shown some increase (∼30%) in wear-life in case of PFPE coated APTMS SAM surfaces whereas this treatment decreased the wear-life in the case of PFPE coated OTS SAM and Si surfaces. The thermally treated PFPE coating onto the APTMS SAM surfaces has shown a wear-life of about ∼7000 cycles, whereas it resulted in a wear-life of about ∼4200 cycles when PFPE is coated onto Si and ∼900 cycles in the case of PFPE coated OTS SAM surfaces.

3.5. Analysis of wear tracks using optical microscopy

Optical micrographs of wear tracks after an appropriate number of sliding cycles for the bare Si, APTMS SAM-modified Si and PFPE-coated APTMS SAM surfaces are
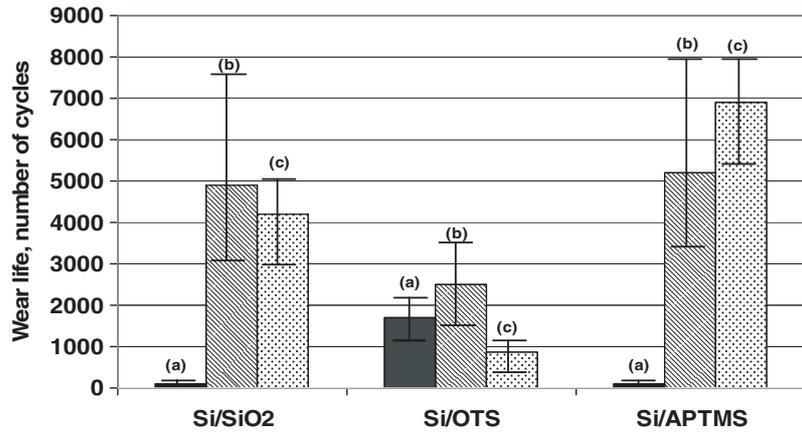
Figure 7. Wear-life, number of cycles of bare Si, OTS SAM and APTMS SAM with and without PFPE overcoat and with thermal treatment after PFPE overcoating. (*a*) No PFPE overcoat, (*b*) PFPE overcoat and (*c*) PFPE overcoat followed by thermal treatment. Data scatter bars are also presented for each case.
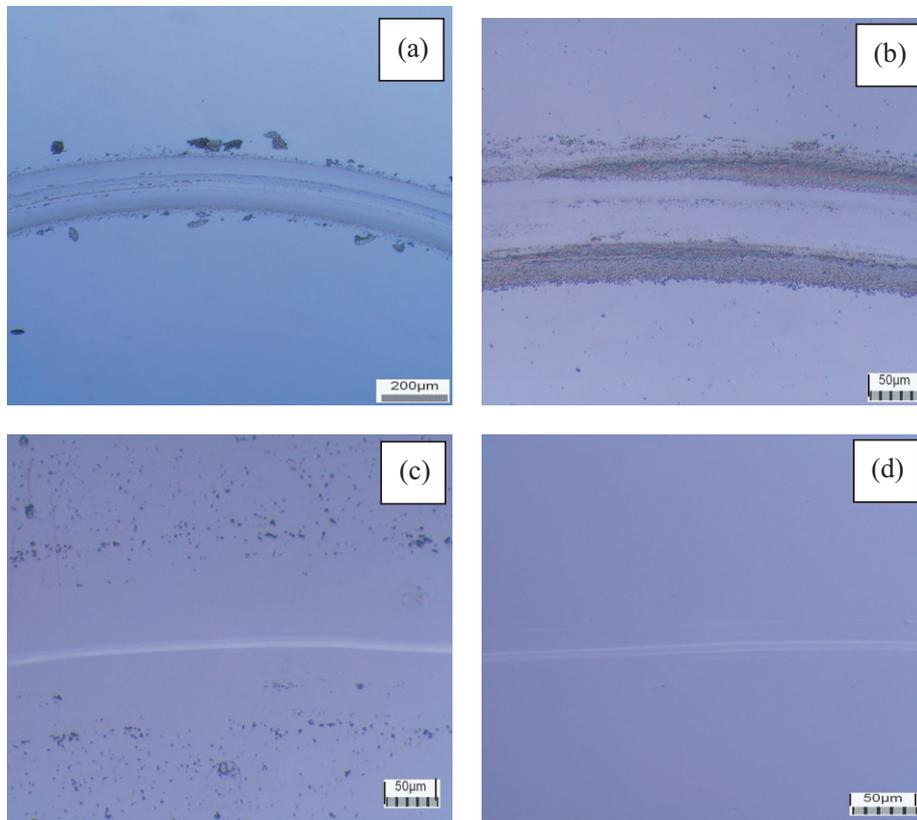

Figure 8. Optical images of the worn surfaces of various samples after appropriate number of cycles of sliding at a contact pressure of 330 MPa, (*a*) bare Si surface after 700 cycles. (*b*) APTMS SAM modified Si sliding after 900 cycles and (*c*) PFPE coated APTMS modified Si after 6000 cycles of sliding. (*d*) Baked-Si/APTMS/PFPE combination after ∼14 000 cycles. Note that the scales used in these figures are much larger than those used in figure 2. This is in order to show microfeatures of the wear tracks after the tests.

shown for comparison in figure 8. After about 700 cycles of sliding on bare Si surface the wear track image shows the accumulation of wear debris along the wear track and severe damage to the Si surface. Even though no chemical analysis of wear debris was carried out, these wear debris must have consisted of the fragments of Si wafer and Si_3N_4 ball. The sharp cornered wear debris must have originated due to the fracture of the Si surface which shows brittle

fracture behaviour. The wear track of the APTMS SAM after 900 cycles also shows the accumulation of the sand-like fine particles along the wear track. These should have originated from the SAM molecules. Further chemical analysis of the wear debris particles was not possible as the spot size of the XPS used is $300\,\mu m \times 700\,\mu m$ which is much larger than the debris size which is $50\,\mu m$ or less. Figure 8(*c*) shows the optical image of the wear track of PFPE-coated APTMS

SAM after about 6000 cycles. We can clearly observe the absence of the wear debris generation and the severe damage to the Si surface. Thermally treated PFPE-coated APTMS SAM surfaces have shown even better performance without any signs of wear to the Si surface until ∼14 000 sliding cycles as evidenced by the optical micrograph shown in figure 8(d). It only shows the signs of initiation of mild scratching inside the wear track. This supports the potential of thermally treated PFPE overcoat on APTMS SAM in enhancing the wear-life. Similar findings are observed for PFPE-coated Si and OTS SAM surfaces as well.

4. Discussion

4.1. Effect of PFPE coating onto bare Si

PFPE coating on Si has shown a coefficient of friction of 0.16 whereas bare Si exhibits 0.6. One of the reasons for the lowering of friction in case of PFPE coated Si is because of the decrease in surface energy [37] and, moreover, because of the flexibility and mobility of the polymer backbone which offers little resistance to sliding [38]. Coefficient of friction of PFPE on Si is comparable with that reported for PFPE on Si surfaces by Ruhe *et al* [34] where the coefficient of friction was reported as 0.18 in a pin-on-disk type of test.

During the wear test bare Si fails within few cycles of sliding. PFPE coating has increased the wear-life of bare Si to around 5000 cycles. This is in good agreement with that reported in the literature [34].

4.2. Tribology of Si/PFPE compared to SAM coated Si surfaces

OTS and APTMS SAMs-modified Si exhibited the coefficient of friction values of 0.18 and 0.5, respectively. APTMS SAM by itself exhibited wear-life comparable to that of bare Si. This is because of their high surface reactivity (hydrophilic nature) which leads to high capillary forces which in turn resulted in high friction and early failure during sliding. OTS SAM by itself has shown higher wear-life of about ∼1600 cycles when compared to the bare Si and APTMS SAM surfaces. PFPE coating onto the Si has shown higher wear-life when compared to only SAM-coated Si surfaces. This is because of the beneficial lubricating properties of PFPE as discussed above. Thus we may conclude that both, coefficient of friction and wear, greatly depend upon the surface energy of the coating. The mobile nature or the inherent lubricity of PFPE molecules may also have added effects on improving the wear-life. This is because, even though the water contact angle for Si/PFPE is much lower (66°) than that for Si/OTS (108°), Si/PFPE give higher wear-life than that for the Si/OTS combination. For Si/APTMS, even though the water contact angle is slightly less (50°) than that for Si/PFPE, the coefficient of friction is much higher with very low wear-life. Thus, the surface energy, as represented by the water contact angle, does not alone explain the variation in the coefficient of friction or wear-life.

4.3. Tribology of SAMs with and without PFPE over coat

As shown in figure 6, the coating of PFPE onto SAM surfaces has reduced the coefficient of friction to about 0.15–0.20. Irrespective of the initial coefficient of friction of SAM surfaces, PFPE coating has shown lower coefficient of friction. This is because once PFPE is deposited on these surfaces, the initial sliding will be between the Si_3N_4 ball and PFPE in all cases. Therefore, the initial surface condition, before PFPE coating, will not influence this friction. The lower coefficient of friction of PFPE is due to the lower resistance offered to the shearing action. The thermal treatment after PFPE coating has further reduced the coefficient of friction.

PFPE overcoating onto the APTMS SAM has shown considerable increase in wear resistance than when it was coated onto the OTS SAM. Without the PFPE overcoat, APTMS SAM has shown higher initial coefficient of friction and failed within few tens of sliding cycles, whereas OTS SAM has shown a wear-life of ∼1600 cycles. After the PFPE coating, APTMS SAM has registered a lower coefficient of friction and did not show failure upto about 5200 cycles whereas PFPE coating onto the OTS SAM has increased its wear-life from 1600 to 2500 cycles. During the sliding of the PFPE-coated SAM surfaces, initially the mobile PFPE molecules are squeezed and displaced out of the contact region. After complete removal of the mobile PFPE from the contact region the hydrogen bonded PFPE, if any, will lubricate the contact. After complete depletion of mobile and bonded PFPE the sliding will be between the ball and SAM molecules and the wear of SAM starts. Hence the PFPE coating onto the SAM surfaces results in the increase in wear resistance.

We speculate that, when PFPE is coated onto SAM surfaces, a part of PFPE is trapped in between SAM molecules, a part is strongly adsorbed through hydrogen bonds and the remaining portion is present as a mobile layer. From the XPS measurements, it is clear that a portion of PFPE is bonded through the hydrogen bonds when PFPE is coated onto the APTMS SAM and bare Si. In the case of APTMS SAM, it is reasonable to expect that a part of the remaining portion of PFPE will be trapped into the defect regions or gaps between various islands of APTMS (refer figure 2) and the remaining portion of PFPE is present as a top mobile layer. In the case of bare Si, all the non-hydrogen bonded PFPE is present as the mobile layer and there is no trapping because of its flat surface. The same argument holds for the OTS SAM surfaces as well because it has shown the featureless surface and, moreover, the density of the OTS SAM molecules is very high which will give less chance for the trapping of any PFPE molecules [39]. We strongly believe that all these three portions (the mobile, the bonded and the trapped PFPE molecules) influence the wear characteristics. This is schematically illustrated in a molecular model shown in figure 9 which is partly based on the model presented by Choi and Kato [40]. The PFPE molecules shown as thick lines on the APTMS SAM surface are those that are strongly adsorbed and thin lines are mobile molecules. The strongly adsorbed molecules act as anchor for the mobile molecules.

The reasons for the higher increase in wear-life in the case of PFPE coating on APTMS SAM is because of the good combination of mobility, entrapment and H-bonding of PFPE. In addition to the mobile portion of PFPE and H-bonded
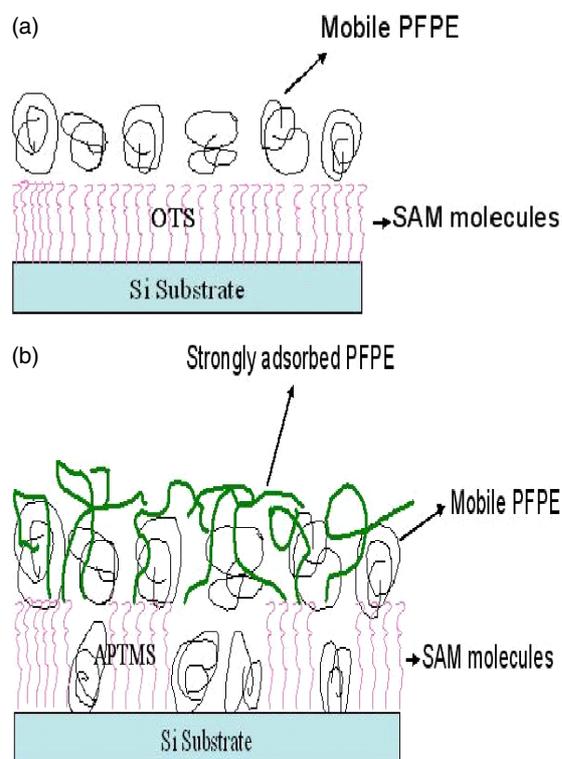
Figure 9. Molecular model of PFPE on (*a*) OTS SAM and (*b*) APTMS SAM (refer text for details). Thicker lines in (*b*) are used for strongly adsorbed and thinner lines for mobile PFPE molecules.

PFPE, the polymer trapped in the gaps between the APTMS molecules provides the additional storage of PFPE molecules, which can reach the surface in a kind of 'squeezing action' when a normal compressive stress is applied. Hence PFPE coating onto the APTMS SAM modified Si has shown higher wear-life compared to all other cases. The entrainment of the mobile PFPE in between the islands of APTMS may be compared with the results of boundary lubrication on etched and textured surfaces [41]. Intentionally created depressions on Si surfaces have shown slightly beneficial results on the coefficient of friction; however, the effect greatly depends upon the hard coating on the Si surface below the lubricant layer and the shape and size of the depressions [41]. The amount of lubricant used in the published work on texturing [41] was much larger than in our case where only a few ($\sim$2 nm) nanometre thick PFPE coating is provided on nanometre thick ($\sim$2–3 nm) SAM layer. The difference between our case and the published work is that the size of the depression between the APTMS islands is much smaller than the textured surface used previously. Also, APTMS has a surface amine group whereas Si contains a hydroxyl group and thus the chemical interactions with PFPE in the two cases would be different. Therefore, we believe that the PFPE entrainment effect in the case of APTMS is different from a simple texturing effect.

The increase in wear-life is very little in the case of the PFPE-coated OTS SAM surfaces because of the absence of bonding between the PFPE and SAM molecules, absence of the trapping of the PFPE molecules inside the SAM, and lower amount of PFPE present. For OTS SAM with low surface energy, it is easier for PFPE molecules to get displaced out of

the wear track during sliding action. Therefore, in the case of the PFPE coating onto the OTS SAM, a small amount of mobile PFPE itself helped to increase the wear-life from 1600 to 2500 cycles.

PFPE coating on bare Si, without any modification, also resulted in good wear-life. The wear-life is almost equal to that of PFPE coated APTMS SAM surfaces. A combination of both mobile and hydrogen bonded PFPE in both cases resulted in higher wear-life. Thus, it appears that the use of SAM as an intermediate layer is not of much significance as only PFPE film on Si also increases the wear-life by several order.

From our results, it may not to be possible to confirm that replenishment characteristics of PFPE contribute to wear-life as the time scale of our test is much faster than the diffusion rate for such an ultra-thin layer of molecules. Choi *et al* [42] and Novotny [43] have reported spreading velocities in the range of few micrometres per second for a non-polar PFPE on the low surface energy molecules/islands such as 1H, 1H, 2H, 2H-perfluorodecyltrichlorosilane (FDTS, CF_3 $(CF_2)_7$ CH_2 CH_2SiCl_3) SAM modified DLC coated magnetic hard disk and polyperfluoropropylene oxide on Si surfaces, respectively. From these two results it is appropriate to assume the spreading velocities of the PFPE to be in the order of few micrometre per second. The time for one revolution during the tribology test in our study is 0.6 s which is slightly lower than the time for the PFPE molecules to migrate back to the wear track. Therefore, we do not expect that the PFPE molecules will help in the lubrication considerably by replenishment of the worn area. Therefore higher increase in the wear-life in the case of PFPE overcoated APTMS SAM and bare Si is due to the strongly bonded PFPE and mobile or/and entrapped PFPE between the SAM islands. Moreover, bonded molecules can also contribute to retaining more of the mobile molecules due to the entanglement between the molecular chains. Fluorinated PFPE molecules are very lubricious due to linear and 'smooth chain profile' as evidenced by the molecular scale friction work carried out by Tabor and co-workers [44] on polytetrafluoroethylene (PTFE), high-density polyethylene (HDPE) and several other polymers. It may be noted that PFPE and PTFE molecules are very similar in the sense that both have common CF_2 chemical group in their back-bone and both have linear molecular structure.

The absence of the wear debris, even after extended cycles of sliding, is one of the advantages with the PFPE coated surfaces which is revealed from the optical micrographs shown in figure 8. The generation of wear debris hinders the smooth operation of the sliding components in MEMS or micro motors and hence coatings which do not generate wear debris are required for running MEMS components up to several millions of cycles at low contact stress conditions [45].

4.4. Effect of thermal treatment

Baking after PFPE coating onto SAMs and bare Si has shown higher water contact angles. There was a considerable increase in water contact angle from 67° to 112° in the case of PFPE-coated Si surface after baking. As reported by Ruhe *et al* [46], the heat treatment procedure of the attached PFPE film on Si surface results in a significant increase of the molecular weight of the polymer through evaporation of lower molecular

weight fractions. Therefore, the thermal treatment might have resulted in the improvement of the density of the polymer film and thus helped in increasing the water contact angle in the case of PFPE coated Si surface.

Further decrease in the coefficient of friction, after baking, is also due to the lowering in the surface energy and due to the increase in the density of the polymer molecules.

Thermal treatment has shown approximately 30% improvement in wear resistance of PFPE coated APTMS SAM. The increase in the percentage of bonded PFPE after thermal treatment for Si/APTMS/PFPE layer is very minimal as seen in figure 5. This might indicate that the thermal treatment in the presence of APTMS does not alter the chemical reactivity between PFPE and the substrate but rather there is some increase in the PFPE density which contributes towards wear-life [46]. Surprisingly, thermal treatment on PFPE coated OTS SAM surface has shown lower wear-life than just OTS modified Si surfaces. Despite the same values of the water contact angle for the cases of APTMS/PFPE and Si/PFPE, there was a little decrease in wear-life after baking of PFPE modified Si surface. While such decreases in the wear-life are well within the experimental data fluctuations, we may note that the contributing factor in decreasing the wear-life could be a reduction in the mobile portion of PFPE after thermal treatment.

5. Conclusions

PFPE is overcoated onto bare Si, APTMS and OTS SAM modified Si surfaces to investigate the effect of the mobile, bonded and thermally treated PFPE on the tribological properties. Sliding tests are carried out on ball-on-disk tribometer using 4 mm diameter Si_3N_4 ball as a counterface at a contact pressure of approximately 330 MPa. The initial coefficient of friction and wear-life, that is the number of cycles after which the film fails are measured during sliding tests.

From this study the following conclusions are drawn:

1. PFPE coating onto the APTMS and OTS SAM surfaces increases their water contact angles and also results in a decrease in the initial coefficient of friction regardless of their initial surface characteristics before PFPE coating.

2. Irrespective of the SAM surface properties PFPE coating increases the wear-life of SAM surfaces. The extent of increase in wear resistance depends on the initial surface conditions such as surface wettability, surface reactivity towards the polar groups of PFPE, molecular packing density and order in the SAM surfaces. Increase in wear-life is much higher when PFPE is coated onto the reactive surfaces such as bare Si and APTMS SAM than when coated onto the non-polar OTS SAM, because of the differences in the extent of bonding between PFPE and SAM molecules.

3. Thermal treatment after PFPE coating on both SAMs and Si surface reduces the coefficient of friction. This treatment enhances the wear-life of PFPE coated APTMS SAM and marginally reduces the wear-life in the case of both OTS SAM and Si surfaces. Overall, thermally treated APTMS/PFPE modified Si surface gives the highest wear-life among the films studied in this work. However, this increase in the wear-life is at best, only approximately 30% over the traditional PFPE-coated Si surface.

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