Microtribological study of perfluoropolyether with different functional groups coated on hydrogen terminated Si

[a]Department of Mechanical Engineering, National University of Singapore, 9 Engineering Drive 1, Singapore 117576

* Corresponding author (e-mail: mpesks@nus.edu.sg)

Myo Minn[a], Nalam Satyanarayana[a], Sujeet K. Sinha[a]* and Hirofumi Kondo[b]

[a]Department of Mechanical Engineering, National University of Singapore, 9 Engineering Drive 1, Singapore 117576, Singapore

*Corresponding author (e-mail: mpesks@nus.edu.sg)

[b]Sony Chemical & Information Device Corporation, R & D Division, 1078 Kamiishikawa Kanuma, 322-8503, Japan

Abstract

Friction and wear properties of different perfluoropolyether (PFPE) films with and without hydrogen termination on Si (Si-H) were studied using a ball-on-disk tribometer. The physical and chemical properties of the films were evaluated using contact angle measurement, atomic force microscopy and X-ray photoelectron spectroscopy. Coating of PFPEs onto bare Si has lowered the coefficient of friction (from 0.6 for Si to ~ 0.05 with PFPE) and enhanced the wear durability (20,000 times) in comparison with those for bare Si which failed immediately. The introduction of hydrogen termination onto Si prior to PFPE coating has further increased the wear durability of PFPE with different functional groups several times (> 5 times) under a normal load of 30 mN and a sliding speed of 0.052 m/s.

1   Introduction

Though Si is currently the most widely used material in micro-electromechanical systems (MEMS) or microsystem devices, its friction and wear performances are extremely poor. Without any surface modification, Si shows high friction, high adhesion and low wear durability. Coatings of organic ultra-thin films (such as self-assembled monolayers (SAMs) or polymer films) on Si have shown good improvements in reducing the coefficient of friction and adhesive forces to a large extent [1-6].

Many organic thin films can effectively reduce friction and adhesion; however, it is observed that their long-term wear resistance is not very significant [1, 7-8] due to a lack of mobile portion of the lubricant. Once wear initiates, the molecules are easily removed from the contact area, the worn particles also act as third body and thus accelerate the wear of the coatings. Therefore, researchers have realized the importance of the mobile portion as the top layer which will give low friction and self-replenishing property due to the migration of mobile molecules into the sliding contact, leading to high wear resistance [1, 3, 5, 9].

Recent studies on PFPE (perfluoropolyether) as a mobile layer with SAMs as intermediate layers on Si have shown good improvement in wear durability [1, 10] with the concept of utilizing SAMs as a good bonding agent between Si substrate and PFPE whereas mobile PFPE being used to lower the friction. Miller et al [9] have investigated the tribological properties of TCP (tricresyl phosphate) coated onto a bound SAM (PFTS – perfluorodecyltrichlorosilane) and observed that the dual-layer film have shown improved wear resistance when compared to only PFTS layer, and the improved tribological properties were attributed to the mobility of TCS. However, as the preparation procedure of SAMs is time-consuming, costly and complicated in many cases, there are some concerns in applying those SAMs on the actual devices. Also, PFPE has been used as both bonded and mobile layers on Si and MEMS device surfaces and it has been observed that an optimum ratio of both bonded and mobile layers of PFPE shows better wear durability over only bonded or only mobile [11]. Therefore, these studies suggested the use of both bonded and mobile layers of lubricant to achieve good tribological properties and especially long term wear durability.

In the present work, we have studied the effectiveness of hydrogen termination on Si as a pre-treatment before dip-coating of PFPE films in enhancing the wear durability of PFPE films. Hydrogen termination is a fast and cost-effective method to create reactive terminal groups. PFPE is chosen because of its low surface tension, chemical and thermal stability, low vapour pressure and good lubricity [12].

2   Experimental procedures

2.1   *Materials and samples preparation*

Polished n-type silicon (100) wafers (of about ~ 0.4 nm roughness) were used as the substrate. The hydrogen-terminated silicon (Si-H) substrates were obtained by immersing cleaned Si substrates into a dilute aqueous solution of hydrofluoric acid (2 vol%) for 30 s. Following this, Si-H substrates were rinsed with distilled water for 1 min and dried with nitrogen gas.

A solution of different PFPE lubricants (Zdol and Zdiac) was dissolved in H-Galden ZV 60 whose structure is $HCF_2O-(CF_2O)p-(CF_2CF_2O)q-CF_2H$. The chemical structures of Zdol and Zdiac, the two lubricants used in this study, are $HO-CH_2CF_2-(O-C_2F_4)p-(O-CF_2)q-OCF_2-CH_2-OH$ and $HO-OC-CF_2-(O-C_2F_4)p-(O-CF_2)q-OCF_2-CO-OH$, respectively. The concentration of the lubricant in the solution for dip-coating was kept as 0.2 wt%. Dip- coating technique was used for lubricant application onto both the bare Si and Si-H samples. The duration of dip-coating time was 30 s with a withdrawal speed of 2.4 mm/s. After dip-coating, the samples were kept in a clean room for 24 h before any test was carried out. The thickness of the lubricant films is about 2 ~ 3 nm as per our previous studies [10, 13]. A schematic diagram of different films on Si is shown in Figure 1.
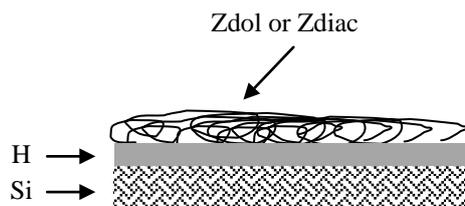
Fig. 1   *A schematic of Zdol or Zdiac attachment to Si-H.*

2.2   Contact angle and surface roughness measurements

VCA Optima Contact Angle System (AST product, Inc., USA) was used for the measurement of contact angles with distilled water droplets. A total of five independent measurements were conducted with a droplet size of 0.5 μL randomly on samples and an average value was taken. The deviation of contact angle was within ± 3°.

The surface roughness of unmodified and modified Si substrates was investigated using an Atomic Force Microscope (Dimension 3000 AFM, Veeco Metrology Inc., Santa Barbara, CA). All images were collected in air using the tapping mode and a silicon tip. The set point voltage used was 1-2 V and the scan rate was 1 Hz.

2.3   XPS analysis

The chemical state of the layers was observed by XPS (x-ray photoelectron spectroscopy) (Kratos Analytical AXIS His). XPS (Al Kα source) tests were performed with an 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. In peak combination, the line width (full width at half-maximum or FWHM) for the Gaussian peaks was maintained constant for all components in a particular spectrum. The curve de-convolution of the obtained XPS spectra was performed by using XPS Peak Fitting Software (XPSPEAK41, Freeware for XPS Community, Chemistry, CUHK).

2.4   Friction and wear tests

Friction and wear tests were carried out on a custom built ball-on-disk microtribometer. A silicon nitride (Si_3N_4) ball of 4 mm diameter with a surface roughness of 5 nm was used as the counterface. The normal load used was 30 mN. The initial coefficient of friction was measured at a sliding track radius of 1 mm with a fixed disc rotational speed of 2 rpm (linear relative speed set at 0.21 mm/s). A lower rotational speed was used to measure the initial coefficient of friction so that the onset of wear can be avoided and the friction response could be mainly arising from molecular interactions. The sampling rate used in recording the data was set at 10 Hz. The wear durability was determined at a fixed disc rotational speed of 500 rpm (linear relative speed was 0.052 m/s) and the friction data were recorded at a sampling rate of 5 Hz. The wear durability was defined as the number of sliding cycles when the coefficient of friction exceeded 0.3 or large fluctuations in the coefficient of friction (indicative of film failure) occurred continuously, whichever happened first. The ambient temperature and the relative humidity were fixed at 25 °C and 65 %, respectively.

3 Results and discussion

3.1 Contact angle and surface roughness

Table 1 summarizes the surface energy data for the Si and Si-H coated with Z-dol and Z-diac films, calculated from the contact angle measurements. The surface energy is divided into dispersive and polar components when we measure the contact angles with both water and n-hexadecane. The difference in surface energy reflects the property of the polar group and the main chain of PFPE. The surface energy of the dispersive and polar components for the bare Si was determined to be 27.5 mJ/m2 and 45.4 mJ/m2, respectively. The total surface energy of the PFPE coated Si surface significantly decreases. The decrease in the surface energy of polar component originates from the adhesive interaction of the functional end group in the upper layer with the polar sites of the underlying surface. Since the PFPE backbone polymer is non-polar and hence will not undergo polar interaction, the observed surface energy decrease results from the interaction of the PFPE polar end groups with the polar entities on the Si surface. This indicates that the polar group is adsorbed on the Si surface with high molecular orientation, and the outermost part is occupied by PFPE chain.

For PFPE coated onto Si-H disks, γ_d(dispersive surface energy) decreases, while γ_p (polar surface energy) increases, this leads to a roughly constant total surface energy value. It is probable that since the functional PFPE interacts differently with the Si-H surface, the molecules in the film tended towards the isotropic orientation. The dispersive and polar surface energy components of Si-H/PFPE infer that the PFPE molecules adsorb on hydrogen terminated Si using dispersive interactions such as through van der Waals interactions and hence lead to more number of hydroxyl groups on the surface. However, these interactions have shown improved tribological properties in the present work which will be discussed in the later sections. The polar hydroxyl or carboxyl group on the outermost surface increases the polar component of the surface energy.

Table 1. *Contact angle and calculated surface energy of differently modified samples.*

Surface	Contact angle (deg)		Surface energy (mJ/m2)		
	Water	Hexadecane	Dispersive	Polar	Total
Si	6	4	27.5	45.4	72.9
Si-Zdol	81	56	16.8	10.3	27.1
Si-Zdiac	85	63	14.6	9.3	23.9
Si-H	71	31	23.8	12.7	36.5
Si-H-Zdol	65	67	13.3	23.6	36.9
Si-H-Zdiac	64	59	15.8	22.4	38.2

Figure 2 shows the topography of unmodified and modified Si surfaces. The AFM images were taken over a scan area of 1 µm x 1 µm. Table 2 provides roughness values and the initial coefficients of friction of Si samples with different modified layers. Bare Si shows a roughness of 0.18 nm. Applying lubricants onto Si increases the roughness to 0.27 nm and 0.29 nm for Si/Zdol and Si/Zdiac, respectively. The modification of Si with hydrogen termination also raises the roughness to 0.28 nm. Further enhancement of roughness is observed when the lubricants are coated onto Si-H, 0.59 nm for Si-H/Zdol and 0.52 nm for Si-H/Zdiac.

| Si | Si/Zdol | Si/Zdiac |

| Si-H | Si-H/Zdol | Si-H/Zdiac |
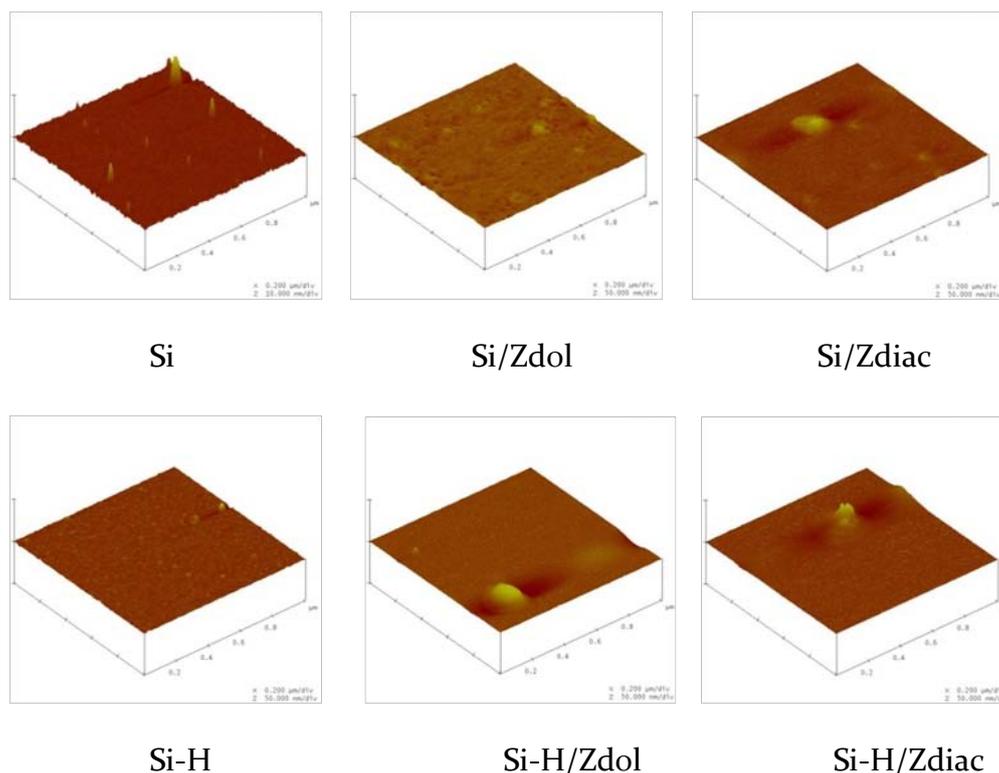
Fig. 2   *AFM images of bare and modified Si surfaces. The scan area for AFM imaging is 1 μm x 1 μm. The vertical scale is 10 nm in all images.*

Table 2. *Roughness and initial coefficient for friction of differently modified samples.*

Surface	Roughness (nm), Ra	Initial coefficient of friction
Si	0.18	0.6
Si-Zdol	0.27	0.07
Si-Zdiac	0.29	0.07
Si-H	0.28	0.3
Si-H-Zdol	0.59	0.05
Si-H-Zdiac	0.52	0.08

3.2   XPS analysis

The chemical analysis of the formed surfaces was carried out by XPS and the wide scan spectra from XPS (not shown) for Si/Zdol and Si/Zdiac showed strong C1s, O1s and F1s peaks, suggesting successful deposition of PFPE molecules on Si substrate. C1s spectrum of Si/Zdol is shown in Figure 3. The existence of the three C1s peaks (O–C–F2, F–C–F, and O–C–F) confirms a successful formation of Zdol film [9, 11]. These three peaks were also observed in the case of Si/Zdiac as well as of Si-H/Zdiac

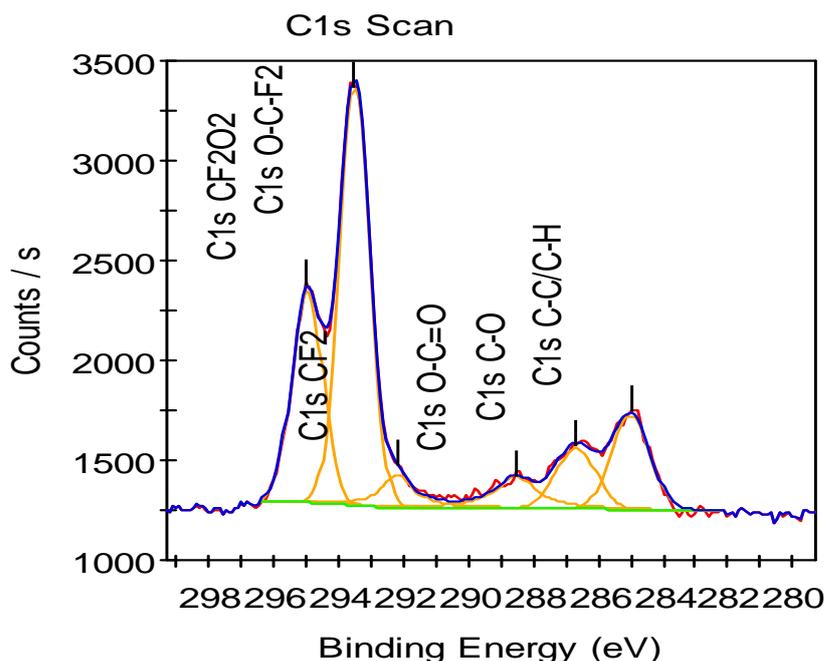because the corresponding chemical groups (O-C-F2, F-C-F and O-C-F) also exist in the backbone of Zdiac.

**Fig. 3**   *High-resolution C1s spectra of Si/Zdol.*

3.3   Tribological results

Table 2 shows the initial coefficient of friction values of unmodified and modified Si surfaces tested at a normal load of 30 mN and a rotational speed of 2 rpm (linear relative speed of 0.21 mm/s). Bare Si has shown a coefficient of friction of 0.6 while Si/Zdol and Si/Zdiac has reduced the coefficient of friction to 0.07, respectively. Bare Si shows high coefficient of friction because of its hydrophilic nature and brittleness. Being hydrophilic, Si attracts more atmospheric water and hence leads to high capillary forces which eventually increase its coefficient of friction. Both Zdol and Zdiac on Si have reduced the coefficient of friction to a very low value (0.07) because of their lubricious nature and low shear strength. Hydrogen termination on Si has also reduced the coefficient of friction of Si to a value of 0.3 (50 percent reduction in the coefficient of friction when compared to that of Si) which is primarily attributed to an increase in the water contact angle (or in other words reduction in the surface energy) which helps in reducing the capillary forces and hence the frictional forces. Si-H/Zdol and Si-H/Zdiac have shown coefficient of friction values as 0.05 and 0.08 respectively, which are similar to those of Si/Zdol and Si/Zdiac. The coefficient of friction values of PFPE films are the same when coated onto Si and Si-H surfaces and the hydrogen termination treatment does not have any effect on the initial coefficient of friction of PFPE films dip-coated onto them. The reason for this behaviour could be the presence of PFPE molecules on all over the surface irrespective of the pre-treatment. Also both Zdol and Zdiac have shown similar coefficient of friction values which must be because of their almost same molecular structure.

The wear durability of Si with different modifications was determined by a ball-on-disk microtribometer and their results are shown in Figure 4. The tests were conducted at 30 mN applied load and 0.052 m/s sliding speed at 25 °C ambient temperature. Bare Si fails within a few cycles whereas hydrogen terminated (Si-H) surface fails in about 100 cycles. The existence of Zdol and Zdiac films with and without hydrogen terminated layer on Si enhanced the wear durability by several orders. PFPE films without any intermediate hydrogen groups extend their wear lives to 20,000 cycles in the case of Si/Zdol and 30,000 cycles in the case of Si/Zdiac. Hydrogen termination on Si provides remarkably high wear durability of more than 100,000 cycles for both Si-H/Zdol and Si-H/Zdiac (the experiments were

stopped at 100,000 cycles because of long hours of testing). Each experiment was repeated at least three times and for each test the wear durability exceeded 100,000 cycles. It is obvious from the above results that the presence of hydrogen termination on Si with either Zdol or Zdiac lubricant has increased the wear durability of bare Si by several orders.

Figure 4 (b) shows the steady state coefficient of friction versus the number of sliding cycles. The coefficient of friction of Si/Zdol is in a range of 0.1 ~ 0.15 and that of Si/Zdiac is about 0.09. After certain number of sliding cycles, their coefficients of friction immediately increase and the films fail as a result of direct interaction between the counterface ball and Si substrate. However, as for Si-H/Zdol and Si-H/Zdiac, the coefficient of friction is below 0.08 for the whole range of the tests and the films do not show any sign of failure until the experiments were stopped (100,000 cycles of sliding).
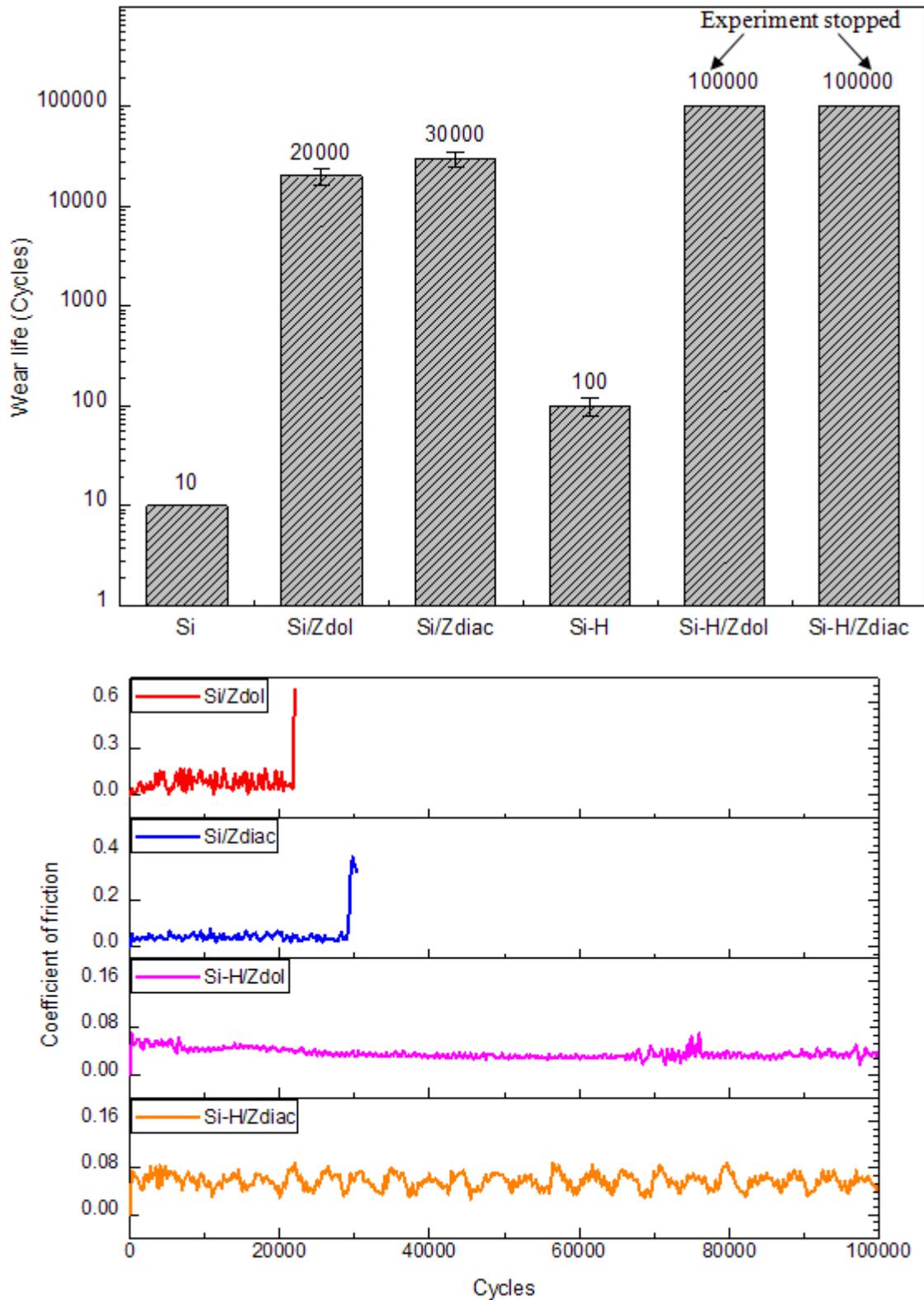
Fig. 4 *(a) Wear durability and (b) coefficient of friction versus number of cycles for differently modified Si samples,*

tested against a 4 mm diameter Si3N4 ball at a normal load of 30 mN and a sliding speed of 0.052 m/s.

Figure 5 shows the optical images of balls and wear tracks on samples after the appropriate numbers of sliding cycles. Both Si/Zdol and Si/Zdiac surfaces had severe wear on the track (after 20,000 and 30,000 sliding cycles, respectively) and wear debris were also clearly observed on their counterface ball. On the other hand, Si-H/Zdol and Si-H/Zdiac samples did not show any sign of wear even after sliding for 100,000 cycles. No wear debris was seen attached to the ball surface in and around the wear

track. Energy dispersive spectroscopy (EDS) (Hitachi S4300 FESEM/EDS system) tests were conducted on the wear tracks in order to confirm the failure of the sample by checking for the presence of Si peak. The EDS analyses of the regions inside and outside the wear track of Si-H/Zdol and Si-H/Zdiac show no or negligible wear to the coated film even after sliding for 100,000 cycles at a normal load of 30 mN.

	Counterface ball	Substrate surface
Si/Zdol		
Si/Zdiac		
Si-H/Zdol		

Si-H/Zdiac
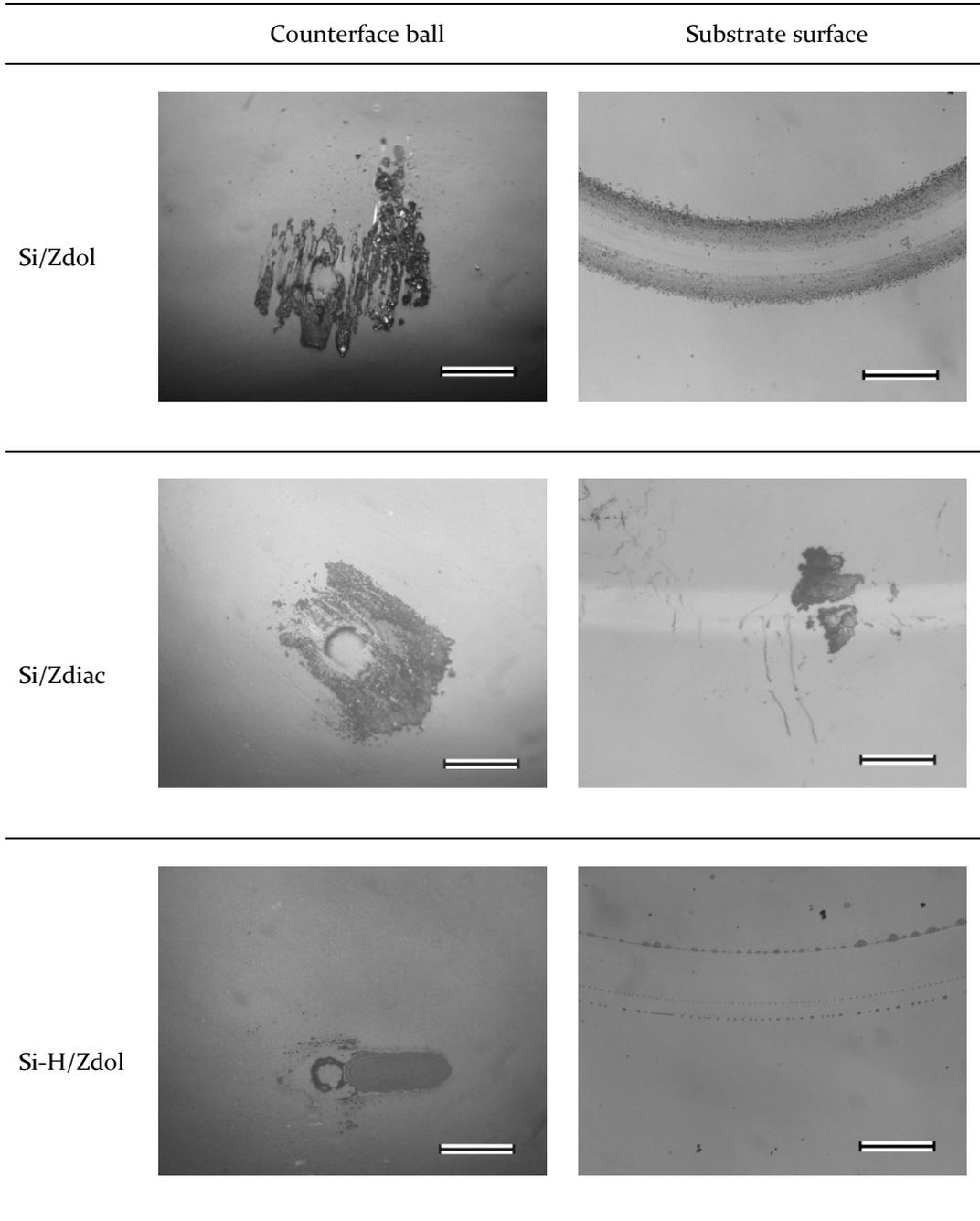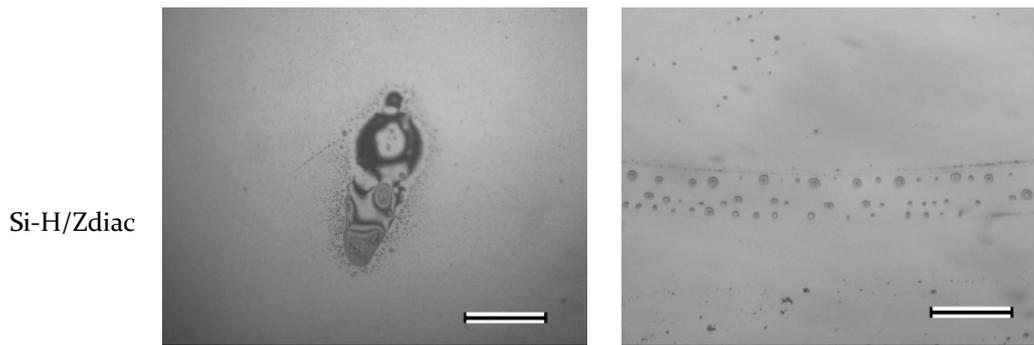
Fig. 5 *Optical images of counterface balls (column 1) slid against different modified Si samples (column 2) after the tests. The optical images of Si/Zdol and Si/Zdiac were taken after 20,000 cycles and 30,000 cycles, respectively when they failed. The optical images of Si-H/Zdol and Si-H/Zdiac were taken after 100,000 cycles of sliding. The scale bars shown in the images are 100 μm.*

The ratios of F/Si evaluated by XPS tests (provided in Table 3) showed a higher ratio for Si-H/Zdol and Si-H/Zdiac when compared with those of Si/Zdol and Si/Zdiac, respectively. It can be deduced that the coverage and the amount of the lubricants (Zdol and Zdiac) on Si substrate seems to have improved with the assistance of hydrogen termination on Si. The better coverage and the higher amounts of lubricants on Si-H must have contributed in increasing the wear durability of Si-H/Zdol and Si-H/Zdiac when compared to the wear durability of Si/Zdol and Si/Zdiac.

Table 3 . *XPS data of different modified Si samples.*

Sample	C	F	Si	F/Si (atom %)
Si/Zdol	20.32	38.45	20.08	1.91
Si-H/Zdol	20.62	46.23	13.8	3.35
Si/Zdiac	20.32	34.58	23.46	1.47
Si-H/Zdiac	20.55	41.33	18.93	2.18

In order to better understand the influence of the chemical bonding/interaction on the wear durability, the top mobile layers of Zdol and Zdiac from Si and Si-H substrates were removed by rinsing in the solvent, ZV 60 and the friction and wear tests were conducted on the bonded/strongly adsorbed layer only. A remarkable difference in wear durability was observed as Si/Zdol (rinsed) and Si/Zdiac (rinsed) surfaces failed within 100 cycles while Si-H/Zdol (rinsed) and Si-H/Zdiac (rinsed) surfaces lasted about 10,000 cycles (tested at a normal load of 30 mN and a sliding speed of 0.052 m/s). These tests conclude that the Si-H surfaces had some effect of hydrogen termination with lower surface energy to high wear durability. After removing the mobile layer from PFPE lubricants, the measured water contact angles did not vary in the case of hydrogen terminated samples (Si-H/Zdol and Si-

H/Zdiac) whereas the water contact angles drop by ~20° for the samples without hydrogen termination (Si/Zdol and Si/Zdiac). These water contact angles data also suggests that the strongly adsorbed portion of the lubricant might be higher for hydrogen terminated Si surface than that for bare Si. In the literature, the chemical reaction between the Si-H surface and hydroxyl/carboxyl groups was used to adsorb self-assembled monolayers onto Si-H surfaces, but these chemical reactions require an aid of either thermal or photochemical energy [14-18]. But, in the present work, a significant amount of chemical adsorption was observed between Si-H and the lubricants which have hydroxyl (Zdol) and carboxyl terminal groups (Zdiac), respectively, without the aid of either thermal or photochemical energy. The exact reason for this behaviour is not clear now and needs a further research on this topic. Also, contrary to the water contact angle observations and wear durability data for the samples after the removal of the mobile PFPE, XPS characterization has shown significantly small amounts of elemental fluorine in both cases of bare Si and Si-H (with both Zdol and Zdiac lubricants). Though the exact reasons are not clear for this observation, one reason could be the non-homogeneity of the lubricants caused by the washing of the lubricants with the ZV 60 solvent. These observations also need further research for clear understanding.

4   Conclusions

In this study, hydrogen terminal groups were introduced onto Si substrate (Si-H) followed by coating of different PFPE films (Zdol and Zdiac). The formation of each layer was confirmed by water contact angle measurement, AFM and XPS analysis. The friction and wear durability of Si with different modified layers were measured with a ball-on-disk microtribometer and the final conclusions are as follows.

1. The water contact angle of Si is 6° and it is highly hydrophilic. Zdol and Zdiac coatings onto bare Si increase the contact angles to 81° and 85° respectively. The surface roughness of bare Si is 0.18 nm but it increases to 0.27 nm for Si/Zdol and 0.29 nm for Si/Zdiac.
2. Hydrogen termination on Si (Si-H) gave a water contact angle of 71° whereas Zdol and Zdiac coated onto Si-H resulted in contact angles of 65° and 64°, respectively. The roughness has also further increased to 0.59 nm for Si-H/Zdol and 0.52 nm for Si-H/Zdiac.
3. The wear durability of Si/Zdol and Si/Zdiac showed a remarkable improvement over that of bare Si. The presence of hydrogen terminal groups on Si (Si-H), further enhanced the wear life of Si-H/Zdol and Si-H/Zdiac to 100,000 cycles when the experiments were stopped (tested at an applied load of 30 mN and a sliding speed of 0.052 m/s). Thus, it is concluded that a simple and cost-effective process of hydrogen termination on Si can be very effective in enhancing its tribological performance when overcoated with different PFPE lubricants.

Acknowledgements

References

[1]   N. Satyanarayana and S.K. Sinha, Tribology of PFPE overcoated self-assembled monolayers deposited on Si surface, Journal of Physics D: Applied Physics. 38 (2005) 3512.
[2]   N. Satyanarayana, S.K. Sinha, and L. Shen, Effect of molecular structure on friction and wear of polymer thin films deposited on Si surface, Tribology Letters 28 (2007) 71-80.
[3]   N. Satyanarayana, K.H. Lau, and S.K. Sinha, Nanolubrication of poly (methyl methacrylate) films on Si for microelectromechanical systems applications, Applied Physics Letters 93 (2008) 261906.
[4]   M. Nakano, T. Ishida, T. Numata, Y. Ando, and S. Sasaki, Tribological behavior of self-assembled double layer measured by a pin-on-plate method, Applied Surface Science 242 (2005) 287-294.

[5]   H-S. Ahn, D. Julthongpiput, D-I. Kim, and V.V. Tsukruk, Dramatic enhancement of wear stability in oil-enriched polymer gel nanolayers, Wear 255 (2003) 801-807.

[6]   D. A. Hook, S. J. Timpe, M. T. Dugger and J. Krim, Tribological degradation of fluorocarbon coated silicon microdevice surfaces in normal and sliding contact, Journal of Applied Physics 104 (2008) 034303.

[7]   V. V. Tsukruk, Nanocomposite polymer layers for molecular tribology, Tribology Letters 10 (1-2) (2001) 127-132.

[8]   V. V. Tsukruk, Molecular lubricants and glues for micro- and nanodevices, Advanced Materials 13 (2001) 95-108.

[9]   B. P. Miller, N. D. Theodore, M. J. Brukman, K. J. Wahl and J. Krim, A nano-to macroscale tribological study of PFTS and TCP lubricants for Si MEMS applications, Tribology Letters 38 (2010) 69-78.

[10]   N. Satyanarayana, N. N. Gosvami, S. K. Sinha and M. P. Srinivasan, Friction, adhesion and wear durability of an ultra-thin perfluoropolyether-coated 3-glycidoxypropyltrimethoxy silane self-assembled monolayer on a Si surface, Philosophical Magazine, 87 (22) (2007) 3209-3227.

[11]   K. C. Eapen, S. T. Patton and J. S. Zabinski, Lubrication of microelectromechanical systems (MEMS) using bound and mobile phases of Fomblin Zdol®, Tribology Letters 12 (2002) 35-41.

[12]   H. Liu and B. Bhushan, Nanotribological characterization of molecularly thick lubricant films for applications to MEMS/NEMS by AFM, Ultramicroscopy 97 (2003) 321-340.

[13]   S. K. Sinha, M. Kawaguchi, T. Kato and F. E. Kennedy, Wear durability studies of ultra-thin perfluoropolyether lubricant on magnetic hard disks, Tribology International 36 (2003) 217-225.

[14]   G. Cleland, B. R. Horrocks and A. Houlton, Direct Functionalization of Silicon via the Self-assembly of Alcohols, Journal of Chemical Society Faraday Transactions 91 (1995) 4001-4003.

[15]   R. Boukherroub, S. Morin, P. Sharpe and D. D. M. Wayner, Insights into the Formation Mechanisms of Si-OR Monolayers from the Thermal Reactions of Alcohols and Aldehydes with Si(111)-H1, Langmuir 16 (2000) 7429-7434.

[16]   Y. J. Li, R. Tero, T. Nagasawa, T. Nagata and T. Urisu, Deposition of 10-undecenoic acid self-assembled layers on H-Si(111) surfaces studied with AFM and FT-IR, Applied Surface Science 238 (2004) 238-241.

[17]   E. J. Lee, T. W. Bitner, J. S. Ha, M. J. Shane and M. J. Sailor, Light-Induced Reactions of Porous and Single-Crystal Si Surfaces with Carboxylic Acids, Journal of the American Chemical Society 118 (1996) 5375-5382.

[18]   H. Asanuma, G. P. Lopinski and H. Z. Yu, Kinetic Control of the Photochemical Reactivity of Hydrogen-Terminated Silicon with Bifunctional Molecules, Langmuir 21 (2005) 5013-5018.