

# Tribo-functionalizing Si and SU8 materials by surface modification for application in MEMS/NEMS actuator-based devices

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## Abstract

Micro/nano-electro-mechanical-systems (MEMS/NEMS) are miniaturized devices built at micro/nanoscales. At these scales, the surface/interfacial forces are extremely strong and they adversely affect the smooth operation and the useful operating lifetimes of such devices. When these forces manifest in severe forms, they lead to material removal and thereby reduce the wear durability of the devices. In this paper, we present a simple, yet robust, two-step surface modification method to significantly enhance the tribological performance of MEMS/NEMS materials. The two-step method involves oxygen plasma treatment of polymeric films and the application of a nanolubricant, namely perfluoropolyether. We apply the two-step method to the two most important MEMS/NEMS structural materials, namely silicon and SU8 polymer. On applying surface modification to these materials, their initial coefficient of friction reduces by  $\sim 4$ – $7$  times and the steady-state coefficient of friction reduces by  $\sim 2.5$ – $3.5$  times. Simultaneously, the wear durability of both the materials increases by  $> 1000$  times. The two-step method is time effective as each of the steps takes the time duration of approximately 1 min. It is also cost effective as the oxygen plasma treatment is a part of the MEMS/NEMS fabrication process. The two-step method can be readily and easily integrated into MEMS/NEMS fabrication processes. It is anticipated that this method will work for any kind of structural material from which MEMS/NEMS are or can be made.

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

## 1. Introduction

MEMS/NEMS tribology is one of the most actively investigated research areas. It is focused on finding robust and reliable solutions to the tribological issues found in miniaturized devices that render them inoperable. At the micro/nanoscales at which the miniaturized devices are built, the surface area-to-volume ratio is very high and hence, surfaces/interface forces such as static friction and dynamic

friction become comparable in magnitude to the forces driving the devices, thereby retarding their motion. These forces in their severe form eventually cause material removal (wear) resulting in the failure of the components. In addition, the materials from which the miniaturized devices are made do not have good tribological properties. This further increases the complexity in solving the tribological issues. Although MEMS/NEMS actuator devices with complex shapes and sizes have been designed, their poor tribological performance has remained the main concern, which has halted their commercialization [1]. To date, commercially successful

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MEMS/NEMS devices have only sensors in them. Therefore, scientists and researchers are greatly interested in solving the tribological issues, as many exciting applications can be attained with devices consisting of moving parts.

In devices/machines, all moving parts need to be lubricated irrespective of their size. At macroscale, conventional solid/liquid lubricants are employed to mitigate friction and wear. However, these conventional lubricants cannot be applied for miniaturized devices, as solid lubricants are about the same size as those of the elements of the devices and conventional liquid lubricants can hardly be used, as they generate liquid-mediated adhesion [2, 3]. Thus, minimizing the surface forces and the occurrence of wear in small-scale mechanical devices is a real challenge.

MEMS/NEMS devices are traditionally made from silicon. The use of silicon as a structural material for the devices is the result of a large amount of process knowledge developed in the semiconductor industries. Silicon is hydrophilic in nature and hence has a high surface energy [4]. It is also brittle and thereby is unable to sustain applied loads (normal and/or shear) [4]. These properties of silicon affect its tribological performance adversely [4]. In order to enhance the tribological performance of silicon, in the past, chemical modification routes such as deposition of thin films/coatings of self-assembled monolayers (SAMs) and diamond-like carbon (DLC) coatings have been investigated [5–8]. Although these coatings can delay the onset of wear, they do not have sufficient wear durability for the required duration of the device operation lifetime. Alternatively, topographical modifications have also been investigated [9, 10]. However, the topographically modified surfaces are susceptible to plastic deformation and early wear, as they experience higher contact pressures. A combined approach of topographical and chemical modification shows better results in terms of reduction in friction property, but the long-term wear durability is again a concern [11]. Recently, vapour phase lubrication technique has shown promising results in enhancing the tribological performance of silicon devices [12].

In recent years, polymeric materials such as SU8 are rapidly replacing silicon as the next-generation MEMS/NEMS structural materials [13–16]. Unlike silicon, SU8 polymer is hydrophobic and biocompatible [13–16]. SU8 can also be fabricated into micro/nanostructures [13–16]. However, SU8 polymer has poor tribological properties [17, 18]. Jiguet *et al* [17, 18] investigated the effect of making nanocomposites and heat treatment on the bulk mechanical and tribological properties of SU8 100  $\mu\text{m}$  thick layers. They measured Young's modulus and fracture strength of the materials by conducting tensile tests, and tribological tests were done by mating the materials against steel and polyoxymethylene (POM) balls. Results showed that there was no improvement in the tribological properties of the nanocomposites when the materials were tested against steel balls. However, the nanocomposites showed a reduction in their friction values by  $\sim 3.5$  times when slid against POM balls, before heat treatment. After heat treatment, the nanocomposites did not show any improvement in their friction property when compared with the unreinforced SU8 material. No direct

correlation was observed between the mechanical properties of the materials and their wear behaviour [17, 18]. It should be noted that, at micro/nanoscales at which the MEMS/NEMS devices operate, surface properties play a dominant role in defining the tribological performance of materials rather than their bulk mechanical properties. In this work, we have undertaken an approach based on surface modification of the MEMS/NEMS materials, namely silicon and SU8 polymer, so as to enhance their tribological properties.

## 2. Experimental

### 2.1. Materials

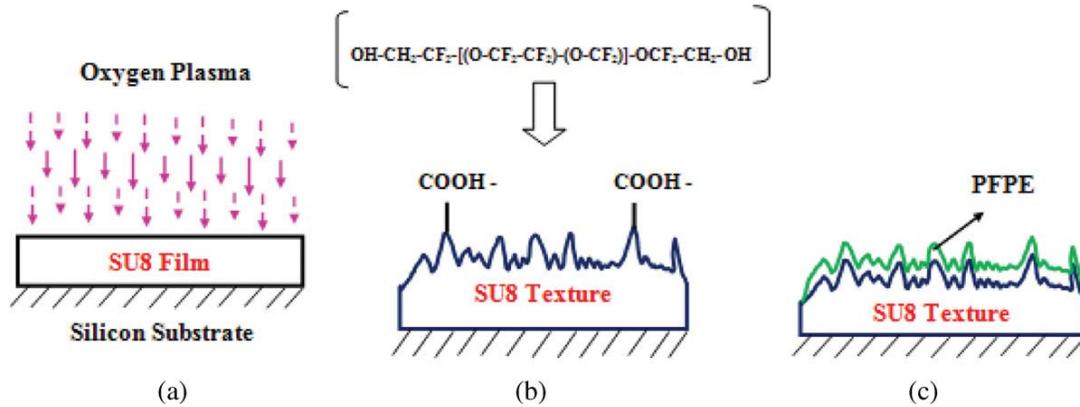
SU8 thin films (thickness  $\sim 500$  nm) were formed on silicon surfaces by spin coating SU8-2000 (Microchem Ltd) on silicon wafers. SU8 thick films (thickness  $\sim 50$   $\mu\text{m}$ ) were formed on silicon surfaces by spin coating SU8-2050 (Microchem Ltd). The speed and duration of spin coating were taken from the supplier Microchem Ltd [19]. The thickness of the spin-coated polymers was measured using a surface profiler (Surface Profiler, P-10 (KLA-Tencor)).

### 2.2. MEMS treatment of SU8 thick films

The SU8 thick films (thickness  $\sim 50$   $\mu\text{m}$ ) were treated with processes similar to those used in the fabrication of actual SU8 MEMS/NEMS components (Recipe: Microchem Ltd [19]). The steps include the following. (i) Pre-baking: the thick films were pre-baked at an initial temperature of 65  $^{\circ}\text{C}$  for a duration of 2 min, followed by an increase in the temperature to 95  $^{\circ}\text{C}$  for a duration of 8 min; (ii) UV exposure: the pre-baked thick films were exposed to UV light (wavelength: 365 nm, power: 210  $\text{mJ cm}^{-2}$ ) using a Mask & Bond Aligner (MA8/BA6, SUSS MicroTec Ltd), for a duration of 30 s; (iii) post-baking: the UV-exposed thick films were post-baked at an initial temperature of 65  $^{\circ}\text{C}$  for a duration of 2 min, followed by an increase in the temperature to 95  $^{\circ}\text{C}$  for a duration of 6 min and (iv) hard-baking: the post-baked thick films were hard-baked at a temperature of 150  $^{\circ}\text{C}$  for a duration of 2 h.

### 2.3. Two-step surface modification method

The two-step surface modification method was applied to the SU8 thin/thick films coated on silicon wafers. In order to enhance the tribological performance of silicon, SU8 thin films (thickness  $\sim 500$  nm) coated on silicon wafers were treated with the two-step method. On the other hand, in order to enhance the tribological performance of SU8 polymer, SU8 thick films (thickness  $\sim 50$   $\mu\text{m}$ ) coated on silicon wafers were treated with the two-step method. Prior to the treatment of the two-step method, the thick polymer films were treated with the processes similar to those that are used in the fabrication of SU8 MEMS/NEMS actuators (micro/nanostructures) [19]. The SU8 thin films were chosen for silicon surfaces as the clearance (gap) between the elements of miniaturized devices is usually a few micrometres [3]. In the case of the SU8 thick films, the thickness of the SU8 polymer films and the MEMS treatments applied to these films rightly represent the size and



**Figure 1.** Schematic showing the two-step surface modification method: (a) exposure of SU8 thin/thick film to O<sub>2</sub> plasma, (b) PFPE coating onto O<sub>2</sub> plasma-treated SU8 thin/thick film and (c) SU8 thin/thick film after O<sub>2</sub> plasma treatment and subsequent PFPE coating.

**Table 1.** Test materials and their nomenclature.

Material	Nomenclature	Material	Nomenclature
Bare Silicon	Si	SU8 thick film (~50 μm) on Si wafer	SU8 ThF
Si coated with PFPE	Si/PFPE	SU8 thick film coated with PFPE	SU8 ThF/PFPE
Si coated with SU8 thin film (~500 nm)	Si/SU8 TF	SU8 thick film treated with O <sub>2</sub> plasma at 25 W	SU8 ThF-O2-25W
Si coated with SU8 thin film and PFPE	Si/SU8 TF/PFPE	SU8 thick film treated with O <sub>2</sub> plasma at 50 W	SU8 ThF-O2-50W
Si coated with SU8 thin film and treated with O <sub>2</sub> plasma at 50 W	Si/SU8 TF-O2-50W	SU8 thick film treated with O <sub>2</sub> plasma at 100 W	SU8 ThF-O2-100W
Si coated with SU8 thin film and treated with O <sub>2</sub> plasma at 100 W	Si/SU8 TF-O2-100W	SU8 thick film treated with O <sub>2</sub> plasma at 25 W and coated with PFPE	SU8 ThF-O2-25W/ PFPE
Si coated with SU8 thin film and treated with O <sub>2</sub> plasma at 50 W and coated with PFPE	Si/SU8 TF-O2-50W/PFPE	SU8 thick film treated with O <sub>2</sub> plasma at 50 W and coated with PFPE	SU8 ThF-O2-50W/PFPE
Si coated with SU8 thin film and treated with O <sub>2</sub> plasma at 100 W and coated with PFPE	Si/SU8 TF-O2-100W/PFPE	SU8 thick film treated with O <sub>2</sub> plasma at 100 W and coated with PFPE	SU8 ThF-O2-100W/ PFPE

the surface/material condition of the real SU8 MEMS/NEMS actuators.

The steps involved in the two-step method are described below:

**Step 1: Oxygen (O<sub>2</sub>) plasma treatment.** The SU8 thin/thick films were exposed to oxygen plasma using a reactive ion etching machine (RIE I Etcher (SIRUS (Trion))). The control parameters during the plasma exposure include O<sub>2</sub> gas flow rate: 10 sccm, pressure: 250 mTorr and time: 1 min. The SU8 thin films were treated with the oxygen plasma at two different power settings, namely 50 and 100 W, while the SU8 thick films were treated at 25, 50 and 100 W.

**Step 2: Perfluoropolyether coating.** After the O<sub>2</sub> plasma treatment, the SU8 thin/thick films were immediately coated with a perfluoropolyether (PFPE) nanolubricant (Fomblin Zdol 4000, Solvay Solexis, Singapore) using a dip coating technique. The samples were dipped into a beaker containing the solution of PFPE (0.5 weight % in H-Galden solvent) for a duration of 1 min, after which they were retracted at a speed of 2.1 mm s<sup>-1</sup>. Figure 1 shows the schematic of the steps involved in the two-step surface modification method.

#### 2.4. Test materials and nomenclature

Table 1 shows the list of the test materials investigated in this work and their nomenclature.

#### 2.5. Surface characterization

The test materials were characterized for their water contact angles (WCA) and nanoscale roughness ( $R_a$ ). The WCA was measured using a VCA Optima contact angle system (AST Products Inc., USA). The WCA measurements were repeated more than ten times to record the most repeatable value. Standard deviations for the data measured were found to be in the range 1–2°. An atomic force microscope (AFM) (Dimension 3000, Digital Instruments, USA) was used to image the surfaces of the test materials. Images of the surfaces (scan area ~1 μm × 1 μm) were recorded in the tapping mode. The images were subsequently analysed to obtain the values of  $R_a$ . For the SU8 thick films, elastic modulus ( $E$ ) and hardness ( $H$ ) were also measured using a nanoindenter system (MTS Nano Indenter XP, MTS Corporation) with a continuous stiffness measurement (CSM) technique. In all CSM tests, a total of ten indents at different random surface locations were performed and averaged to determine the mean hardness and elastic modulus values.

**Table 2.** Surface properties of the test materials.

Material	WCA (deg)	$R_a$ (nm)	Material	WCA (deg)	$R_a$ (nm)	$E$ (GPa)	$H$ (GPa)
Si	12	0.20	SU8 ThF	94	0.26	4.0	0.35
Si/PFPE	66	0.60	SU8 ThF/PFPE	100	0.29	4.0	0.36
Si/SU8 TF	75	0.20	SU8 ThF-O2-25W	~ 6	4.87	4.1	0.36
Si/SU8 TF/PFPE	87	0.21	SU8 ThF-O2-50W	~ 5	9.13	4.2	0.31
Si/SU8 TF-O2-50W	<5	4.80	SU8 ThF-O2-100W	<5	12.86	3.2	0.17
Si/SU8 TF-O2-100W	<5	9.23	SU8 ThF-O2-25W/PFPE	59	4.65	4.1	0.36
Si/SU8 TF-O2-50W/PFPE	79	6.80	SU8 ThF-O2-50W/PFPE	68	7.01	3.8	0.28
Si/SU8 TF-O2-100W/PFPE	92	15.60	SU8 ThF-O2-100W/PFPE	79	8.22	3.0	0.16

Note: WCA: water contact angle,  $R_a$ : roughness,  $E$ : elastic modulus and  $H$ : hardness. WCA was measured using the sessile drop method.  $R_a$  values were measured using an atomic force microscope (AFM). Mechanical properties ( $E$  and  $H$ ) were measured using a nanoindenter system.

## 2.6. Tribological characterization

Tribological tests were conducted using a Micro-Tribo Tester in a ball-on-disc configuration (UMT-2, CETR Inc, USA). The test materials were mated against 4 mm diameter silicon nitride ( $\text{Si}_3\text{N}_4$ ) balls and were made to slide under an applied normal load of 0.3 N at a speed of 200 rpm ( $\sim 42 \text{ mm s}^{-1}$ ). The friction coefficients of the samples were recorded as a function of number of sliding cycles ( $n$ ). The number of cycles ( $n$ ) indicates quantitatively the wear durability of the surfaces (wear life). Experiments were stopped when the surfaces of the test materials showed evidence of surface failure (coefficient of friction  $>0.3$  and/or traces of wear at the surfaces with fluctuating friction values). The initial coefficient of friction ( $\mu_i$ ) was measured from the recorded plot of coefficient of friction versus number of sliding cycles ( $n$ ), at the duration of  $\sim 6$  cycles. The steady-state coefficient of friction ( $\mu_s$ ) was measured at the number of cycles ( $n$ ) at which the material showed stable friction characteristics. Depending on the performance of the test materials, some test materials were further subjected to tribological tests at higher applied normal loads of 0.8, 1 and 1.5 N. All tests were conducted under the ambient conditions of temperature  $24^\circ\text{C}$  and at 65% relative humidity. Contact pressures were estimated using the Hertzian model [20]. After tribological tests, the surfaces of the test materials and counterface balls were observed under an optical microscope. Images showing the occurrence of wear (if any) were recorded. These images qualitatively showed the amount of material removed from the surfaces of the test materials.

## 3. Results and discussion

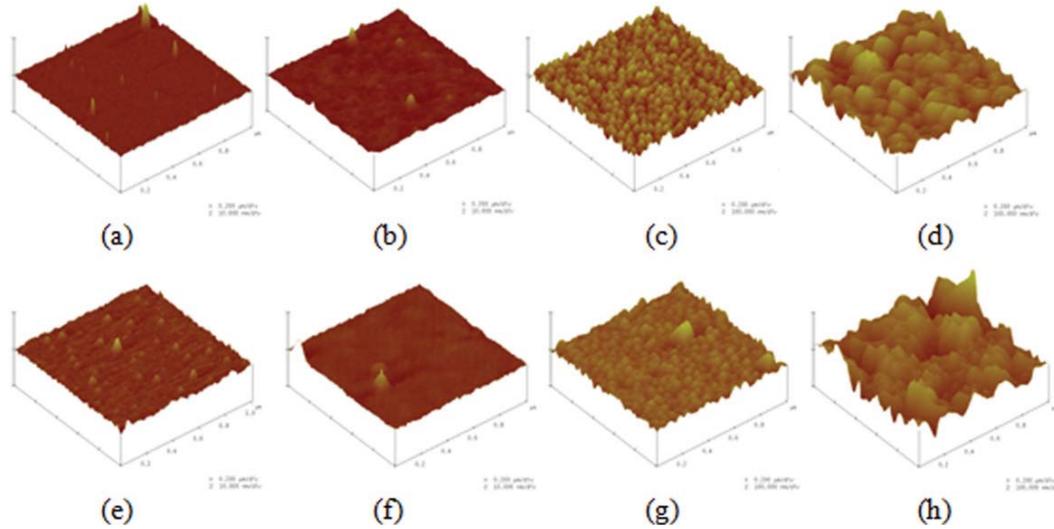
### 3.1. Silicon and modified silicon surfaces

Table 2 shows the WCA values of Si and modified Si surfaces. Si is hydrophilic (WCA  $\sim 12^\circ$ ), whereas the Si/PFPE and Si/SU8 TF surfaces are semi-hydrophobic. The Si/SU8 TF/PFPE surface is nearly hydrophobic (WCA  $\sim 87^\circ$ ). The plasma-treated surfaces, namely Si/SU8 TF-O2-50W and Si/SU8 TF-O2-100W, show hydrophilic property with WCA  $< 5^\circ$ . The hydrophilic nature of these surfaces is attributed to the creation of active/polar carboxyl functional groups ( $-\text{COOH}$ ) [21]. Walther *et al* in their work on making polymeric surfaces hydrophilic for applications related

to bio-MEMS and microfluidic devices have reported the formation of these active chemical groups on SU8 polymeric films treated with  $\text{O}_2$  plasma, through x-ray photoelectron spectroscopy (XPS) studies [21]. From table 2, it can be seen that upon coating with PFPE the plasma-treated surfaces (Si/SU8 TF-O2-50W/PFPE, Si/SU8 TF-O2-100W/PFPE) become semi-hydrophobic and hydrophobic, respectively. PFPE when coated onto any surface increases the WCA value, owing to the presence of fluorine atoms in its molecular structure [22].

Table 2 also shows the  $R_a$  values of Si and modified Si surfaces. Figure 2 shows the AFM images of these surfaces. Si surface is atomically flat ( $R_a \sim 0.2 \text{ nm}$ ). The Si/PFPE surface shows a roughness value of  $\sim 0.6 \text{ nm}$ . The Si/SU8 TF and Si/SU8 TF/PFPE surfaces show  $R_a$  values similar to that of the Si surface. The plasma-treated surfaces, namely Si/SU8 TF-O2-50W and Si/SU8 TF-O2-100W, show roughness values ( $R_a \sim 4.8 \text{ nm}$  for 50 W,  $R_a \sim 9.2 \text{ nm}$  for 100 W) that are higher by an order of magnitude when compared with that of the Si/SU8 TF surface. The presence of nanoscale roughness on the plasma-treated surfaces and the increase in their  $R_a$  value with the intensity of the plasma (power) is due to the etching effect of the energetic plasma. Such an occurrence has been reported earlier on  $\text{O}_2$ -treated SU8 polymer films [21, 23]. In the present case, the Si/SU8 TF-O2-50W/PFPE and Si/SU8 TF-O2-100W/PFPE surfaces show higher values of roughness,  $R_a \sim 6.8 \text{ nm}$  and  $R_a \sim 15.6 \text{ nm}$ , respectively. The higher values of  $R_a$  and the presence of PFPE overcoat in these two materials give rise to their semi-hydrophobic and hydrophobic property.

Figure 3 shows the tribological test results of Si and modified Si surfaces at the applied normal load of 0.3 N (Si: Hertzian contact pressure  $\sim 612 \text{ MPa}$ ). Figure 3(a) shows the coefficient of friction as a function of the number of sliding cycles ( $n$ ) of Si, Si/PFPE, Si/SU8 TF and Si/SU8 TF/PFPE surfaces. From this figure it can be seen that the Si surface exhibits very high values of coefficients of friction ( $\mu_i \sim 0.75$ ,  $\mu_s \sim 0.7$ ) and very low wear durability ( $n < 100$  cycles). Si is hydrophilic in nature and hence it supports high capillary force, which causes very high  $\mu_i$  values through capillary-induced adhesion [4]. Capillary force occurs as a result of water condensation from the environment that leads to the formation of meniscus bridge [3]. Furthermore,



**Figure 2.** AFM images of (a) Si, (b) Si/SU8 TF, (c) Si/SU8 TF-O2-50W, (d) Si/SU8 TF-O2-100W, (e) Si/PFPE, (f) Si/SU8 TF/PFPE, (g) Si/SU8 TF-O2-50W/PFPE and (h) Si/SU8 TF-O2-100W/PFPE surfaces. The scan area of the images is  $\sim 1 \mu\text{m} \times 1 \mu\text{m}$ . The vertical scale is 10 nm for the images shown in (a), (b), (e) and (f) and 100 nm for the remaining images.

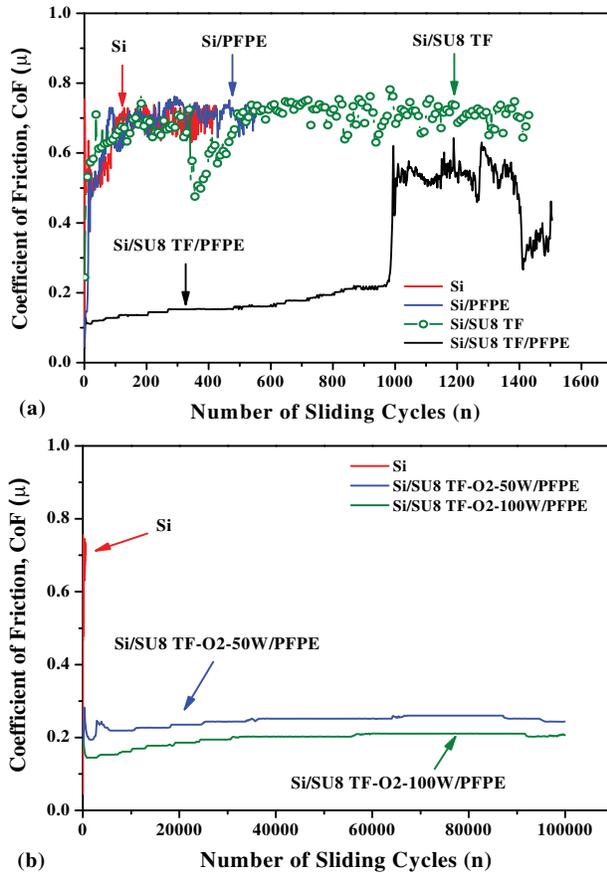
Si is brittle and undergoes wear easily; thereby it exhibits very high  $\mu_s$  values and very low wear durability [4]. The poor performance of Si makes it unsuitable for tribological applications in miniaturized devices unless its surface is modified and improved tribologically.

Coating of Si surface with PFPE (Si/PFPE) shows good improvement in frictional properties ( $\mu_i \sim 0.15$ ,  $\mu_s \sim 0.17$ ); however, the surface has a low wear durability ( $n < 100$  cycles). The Si/SU8 TF surface shows very high friction coefficients ( $\mu_i \sim 0.55$ ,  $\mu_s \sim 0.73$ ), and very low wear durability ( $n < 100$  cycles). The SU8 polymer has low plastic deformation due to extensive cross-linking. Therefore, it gets easily removed under shearing loads and exhibits high frictional properties [17]. The plasma-treated surfaces (Si/SU8 TF-O2-50W, Si/SU8 TF-O2-100W) show very high frictional values of  $\mu_i \sim 0.66/0.57$  and  $\mu_s \sim 0.75/0.65$ , respectively. Both the surfaces have very low wear durability ( $n < 100$  cycles). The hydrophilic nature of these surfaces makes them susceptible to large capillary forces and adhesion that give rise to high frictional values. In addition, the surfaces have high roughness and in the absence of surface protection, such as through PFPE nanolubricant, they easily undergo wear. The Si/SU8 TF/PFPE surface shows low values of coefficients of friction ( $\mu_i \sim 0.15$ ,  $\mu_s \sim 0.24$ ) and high wear durability ( $n \sim 1000$  cycles). Although this surface exhibits better tribological properties, it should be noted that in real time MEMS/NEMS actuators are expected to run smoothly for several thousands of cycles, and therefore its tribological performance is not up to the requirement in terms of application.

Figure 3(b) shows the tribological test results of the Si surfaces treated with the two-step method (Si/SU8 TF-O2-50W/PFPE, Si/SU8 TF-O2-100W/PFPE) in comparison with that of Si. It can be seen from this figure that the modified Si surfaces show excellent tribological properties. The Si/SU8 TF-O2-50W/PFPE surface exhibits low coefficients of friction values ( $\mu_i \sim 0.28$ ,  $\mu_s \sim 0.25$ ), which are  $\sim 2.6$  and  $2.8$  times

lower than those of Si, respectively. Similarly, the Si/SU8 TF-O2-100W/PFPE surface shows low coefficients of friction values ( $\mu_i \sim 0.18$ ,  $\mu_s \sim 0.20$ ), which are  $\sim 4$  and  $3.5$  times lower than those of Si, respectively. Both the modified surfaces show high wear durability ( $n > 100\,000$  cycles), which is  $>1000$  times higher than that of Si. For the Si surfaces treated with the two-step method the tests were stopped at  $\sim 100\,000$  cycles, due to long test duration ( $\sim 8$  h). The low  $\mu_i$  values of the Si surfaces modified with the two-step method are due to their semi-hydrophobic and hydrophobic nature, reduced contact areas (considering the surface roughness) and the lubrication effect of PFPE nanolubricant. The reduction in the interfacial shear strength brought forth by the lubrication effect of PFPE leads to the low  $\mu_s$  values for these modified surfaces. PFPE is an excellent nanolubricant [22, 24–26], and is being used in magnetic recording media to lubricate the interface between the head and disk/tape [27].

To understand the reason for the excellent durability of the materials modified by the two-step method, we compare the durability of the surfaces with that of the Si/SU8 TF/PFPE surface, and observe that the former outperform the latter by two orders of magnitude ( $>100$  times). In the Si/SU8 TF/PFPE surface, the nanolubricant is applied over the regular SU8 thin film, whereas in Si/SU8-O2-50W/PFPE and Si/SU8-O2-100W/PFPE surfaces, the nanolubricant is coated over chemically active SU8 thin films. The molecules of PFPE nanolubricant have hydroxyl ( $-\text{OH}$ ) groups at both their terminal ends (PFPE:  $\text{OH}-\text{CH}_2-\text{CF}_2-[(\text{O}-\text{CF}_2-\text{CF}_2)_p-(\text{O}-\text{CF}_2)_q]-\text{OCF}_2-\text{CH}_2-\text{OH}$ ), and the  $\text{O}_2$  plasma-treated SU8 thin film surfaces have carboxyl functional groups ( $-\text{COOH}$ ) [21]. As both the PFPE molecules and the  $\text{O}_2$  plasma-treated SU8 thin film surfaces have polar reactive chemical groups, strong chemical bonds are expected to form between them [28, 29]. For this reason, PFPE molecules get anchored strongly onto the SU8 thin film surfaces, thereby resisting their removal under shear loading, which increases their durability.



**Figure 3.** Coefficient of friction as a function of number of sliding cycles ( $n$ ) for (a) Si, Si/PFPE, Si/SU8 TF and Si/SU8 TF/PFPE surfaces, and (b) Si, Si/SU8 TF-O2-50W/PFPE and Si/SU8 TF-O2-100W/PFPE surfaces, tested against 4 mm diameter  $\text{Si}_3\text{N}_4$  balls at a normal load of 0.3 N and a sliding speed of  $\sim 42 \text{ mm s}^{-1}$ . For Si surfaces treated with the two-step method the tests were stopped at  $\sim 100\,000$  cycles, due to long test duration ( $\sim 8 \text{ h}$ ).

On comparing the performance of the Si surfaces modified by the two-step method and those modified by the conventional coatings, the latter show lower wear durability by  $\sim 2$ – $3$  orders of magnitude [22, 30]. For example, Si surfaces coated with octadecyltrichlorosilane (OTS) SAM showed durability that was lower by  $\sim 2$  orders of magnitude ( $n \sim 1600$  cycles), even at a load that was 6 times lower and at a speed that was 2 times lower than the ones used in this work [22]. Furthermore, Si surfaces coated with a DLC thin film coating ( $\sim 50 \text{ nm}$  thick) showed durability that was lower by  $\sim 3$  orders of magnitude ( $n \sim 400$  cycles), even at a load that was 7.5 times lower than the one used in this work, but at a speed that was 2 times higher [30].

Figure 4 shows the optical micrographs of the worn surfaces of the test materials and their counterface balls, taken after the tests. Within a very short duration of the test, Si undergoes severe wear (figure 4(a)) with considerable material removed from its surface and transferred to its counterface ball (figure 4(g)). Severe wear was also observed in Si/PFPE, Si/SU8 TF and Si/SU8 TF/PFPE surfaces. The Si surfaces modified by the two-step method (i.e. surfaces Si/SU8

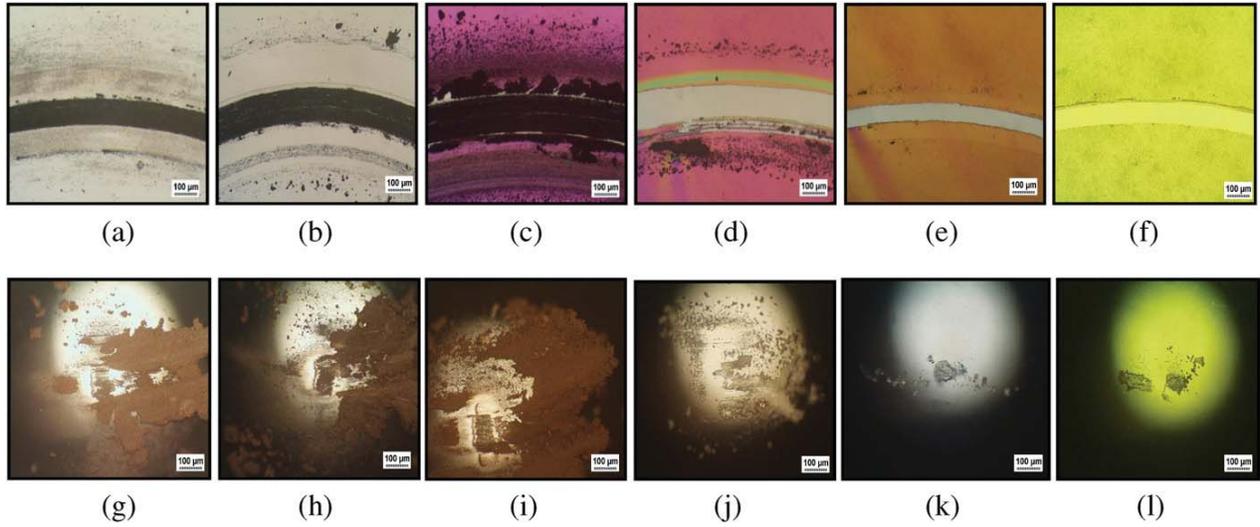
TF-O2-50W/PFPE, Si/SU8 TF-O2-100W/PFPE) show only sliding marks on their surfaces with no recognizable wear even after  $\sim 100\,000$  cycles of sliding (figure 4(e) and (f)). The material transfer is also minimal, possibly consisting of mobile PFPE molecules picked up from the surfaces during sliding (figure 4(k) and (l)). Thus, it is seen that by applying the two-step method to Si, its tribological performance can be enhanced significantly through the reduction in its frictional properties,  $\mu_i$  and  $\mu_s$ , by  $\sim 2.6$ – $2.8$  times and by  $\sim 3.5$ – $4$  times, respectively, and simultaneously increasing its durability by  $> 1000$  times, indicating that the two-step method is an excellent tribological solution for Si-based miniaturized devices.

### 3.2. SU8 polymer and modified SU8 surfaces

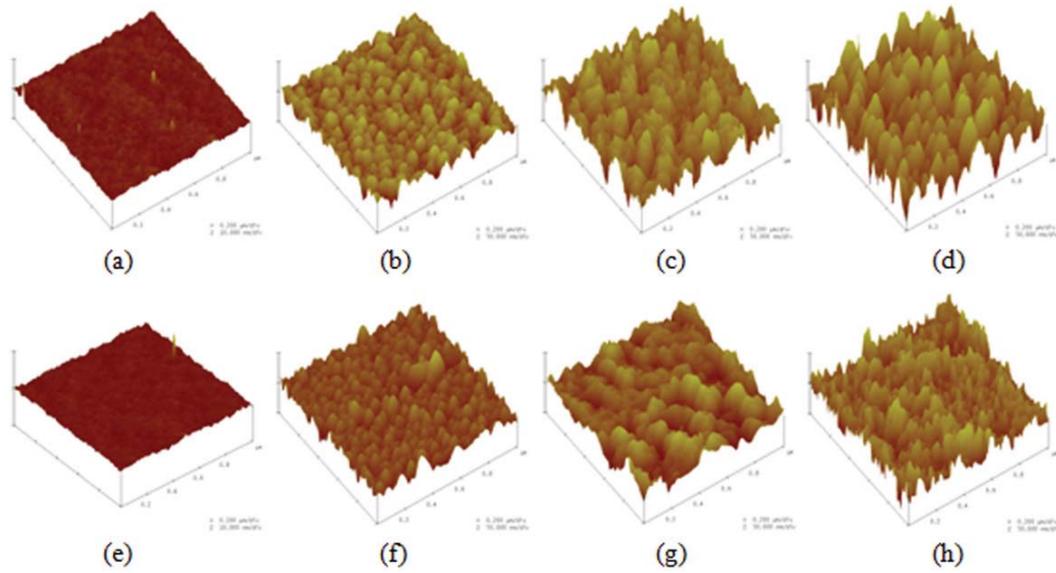
Table 2 shows the WCA values of the SU8 ThF and modified SU8 thick films. SU8 ThF surface is hydrophobic (WCA  $\sim 94^\circ$ ). The SU8 ThF/PFPE surface shows an increased WCA of  $\sim 100^\circ$ . The plasma-treated surfaces (SU8 ThF-O2-25W, SU8 ThF-O2-50W and SU8 ThF-O2-100W) are hydrophilic (WCA  $\leq 6^\circ$ ). The hydrophilic nature of these surfaces is attributed to the presence of active/polar carboxyl functional groups ( $-\text{COOH}$ ) on their surfaces [21]. From table 2, it can be seen that upon coating with PFPE the plasma-treated surfaces (SU8 ThF-O2-25W/PFPE, SU8 ThF-O2-50W/PFPE and SU8 ThF-O2-100W/PFPE) become semi-hydrophobic.

Table 2 also shows the  $R_a$  values of the SU8 ThF and modified SU8 thick film surfaces. Figure 5 shows the AFM images of these surfaces. The SU8 ThF surface has a  $R_a$  of  $\sim 0.26 \text{ nm}$  and when coated with PFPE (SU8 ThF/PFPE surface) it shows a slight increase in the  $R_a$  value ( $\sim 0.29 \text{ nm}$ ). The plasma-treated surfaces (SU8 ThF-O2-25W, SU8 ThF-O2-50W and SU8 ThF-O2-100W) show roughness values ( $R_a \sim 4.87 \text{ nm}$  for 25 W,  $R_a \sim 9.13 \text{ nm}$  for 50 W and  $R_a \sim 12.86 \text{ nm}$  for 100 W) that are higher by an order of magnitude when compared with that of the SU8 ThF surface. The  $R_a$  values of these surfaces increase with the intensity of the applied plasma (power) due to the etching effect of the energetic plasma [21, 23]. The SU8 thick films modified by the two-step method (SU8 ThF-O2-25W/PFPE, SU8 ThF-O2-50W/PFPE and SU8 ThF-O2-100W/PFPE) show slightly lower values of roughness ( $R_a \sim 4.65 \text{ nm}$ ,  $R_a \sim 7.01 \text{ nm}$  and  $R_a \sim 8.22 \text{ nm}$ , respectively), when compared with the SU8 thick films treated with plasma. This could be understood by considering the fact that when the PFPE nanolubricant is coated onto the plasma-treated surfaces, the PFPE molecules would get deposited in the valleys of the rough surfaces, resulting in a slight reduction in the overall roughness values.

Table 2 shows the data of the nanomechanical properties (elastic modulus,  $E$ , and hardness,  $H$ ) of the SU8 ThF and modified SU8 thick films. From the table, it could be seen that the  $E$  and  $H$  values of the SU8 ThF do not show any significant change upon being coated with PFPE nanolubricant. However, when the SU8 ThF surface is exposed to the plasma at lower intensities, the  $E$  and  $H$  values slightly increase, probably due to cross-linking within the polymer surface. With an increase



**Figure 4.** Optical micrographs of worn surfaces: (a) Si (at ~400 cycles), (b) Si/PFPE (at ~550 cycles), (c) Si/SU8 TF (at ~1400 cycles), (d) Si/SU8 TF/PFPE (at ~1500 cycles), (e) Si/SU8 TF-O<sub>2</sub>-50W/PFPE (at ~100 000 cycles) and (f) Si/SU8 TF-O<sub>2</sub>-100W/PFPE (at ~100 000 cycles). Images (g), (h), (i), (j), (k) and (l) are optical micrographs of the surfaces of counterface balls corresponding to the worn surfaces shown in (a), (b), (c), (d), (e) and (f), respectively. The scale bar is 100 μm in all the images.

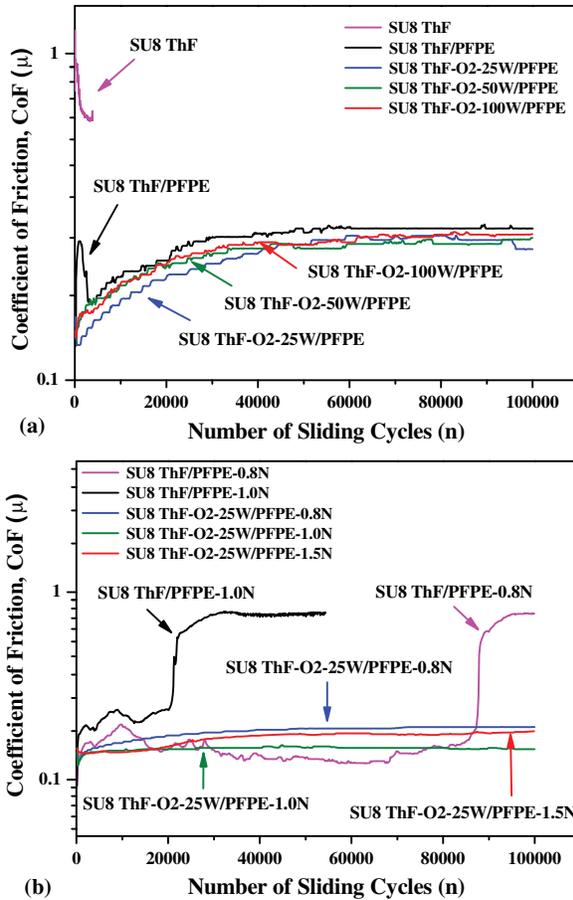


**Figure 5.** AFM images of (a) SU8 ThF, (b) SU8 ThF-O<sub>2</sub>-25W, (c) SU8 ThF-O<sub>2</sub>-50W, (d) SU8 ThF-O<sub>2</sub>-100W, (e) SU8 ThF/PFPE, (f) SU8 ThF-O<sub>2</sub>-25W/PFPE, (g) SU8 ThF-O<sub>2</sub>-50W/PFPE and (h) SU8 ThF-O<sub>2</sub>-100W/PFPE surfaces. The scan area of the images is ~1 μm × 1 μm. The vertical scale is 10 nm for the images shown in (a) and (e) and 50 nm for the remaining images.

in the intensity of the plasma, the  $E$  and  $H$  values reduce, which may be due to the increased etching of the surfaces (increased  $R_a$  values). Upon coating the PFPE nanolubricant to the plasma-treated samples, the  $E$  and  $H$  values do not change for the surfaces treated with the plasma at lower intensities, whereas the values considerably decrease for the surfaces treated with the plasma at higher intensities. This observation indirectly indicates that a greater amount of PFPE material might be present on the surfaces of the SU8 thick films treated with the plasma at higher intensities. With the increase in the plasma intensity, the wettability increases (reduction in WCA values) and also the roughness increases by ~3 times

(increase in the availability of more area at the valleys of the rough surfaces), resulting in a large amount of PFPE deposition at the surfaces.

Figure 6(a) shows the tribological test results of the SU8 ThF and modified SU8 thick films at the applied normal load of 0.3 N (SU8 thick film: Hertzian contact pressure ~ 63 MPa). From this figure it can be seen that the SU8 ThF exhibits very high values of the coefficients of friction ( $\mu_i \sim 1.22$ ,  $\mu_s \sim 0.64$ ) and very low wear durability ( $n < 100$  cycles). The extensive cross-linking in the SU8 polymer due to UV curing and heat treatments restricts plastic deformation. Hence, SU8 gets easily removed under shearing loads and exhibits high



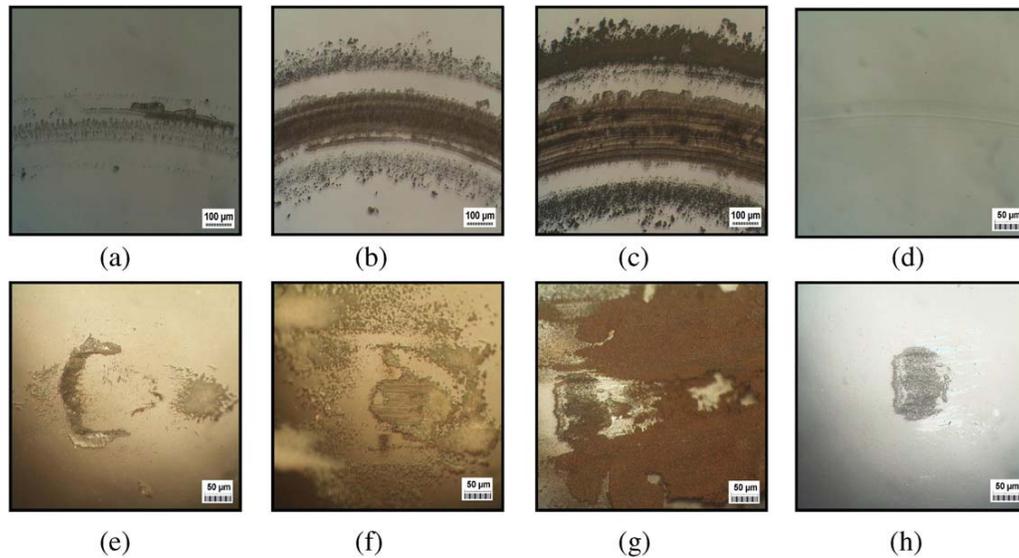
**Figure 6.** Coefficient of friction as a function of number of sliding cycles ( $n$ ) for (a) SU8 ThF, SU8 ThF/PFPE, SU8 ThF-O2-25W/PFPE, SU8 ThF-O2-50W/PFPE and SU8 ThF-O2-100W/PFPE surfaces, tested at a normal load of 0.3 N, and (b) for SU8 ThF/PFPE surface (at normal loads of 0.8 N and 1 N, respectively) and SU8 ThF-O2-25W/PFPE surface (at normal loads of 0.8 N, 1 N and 1.5 N, respectively). For SU8 thick films treated with the two-step method the tests were stopped at  $\sim 100\,000$  cycles, due to long test duration ( $\sim 8$  h).

frictional properties [7]. Figures 7(a) and (e) show the optical micrographs of the worn surface of SU8 ThF and the material transferred to its counterface ball, respectively, indicating early failure. The poor tribological performance of the SU8 thick film is unsuitable for miniaturized devices and therefore, its surface requires modification to perform acceptably under tribological contact. Furthermore, the SU8 thick films treated with  $O_2$  plasma (SU8 ThF-O2-25W, SU8 ThF-O2-50W and SU8 ThF-O2-100W) also show very high frictional properties, with all the three surfaces showing  $\mu_i \sim 1$  and  $\mu_s \sim 1.2$ . These surfaces also have very low wear durability ( $n < 100$  cycles). The hydrophilic nature of these surfaces supports large capillary forces which cause high frictional properties due to surface adhesion. In addition, the surfaces have high roughness and in the absence of surface protection, such as through PFPE nanolubricant, they easily undergo brittle fracture resulting in wear.

Coating of SU8 ThF surfaces with PFPE (SU8 ThF/PFPE) shows significant improvement in the frictional properties

( $\mu_i \sim 0.1$ ,  $\mu_s \sim 0.29$ ), which are  $\sim 12$  and 3.2 times lower than those of the SU8 ThF surface, respectively. The SU8 ThF/PFPE surface shows low values of coefficients of friction ( $\mu_i$  and  $\mu_s$ ), due to its hydrophobic property and the lubrication effect of PFPE. It also shows high wear durability ( $n > 100\,000$  cycles), which is  $> 1000$  times higher than that of the SU8 ThF surfaces. The SU8 thick films modified by the two-step method (SU8 ThF-O2-25W/PFPE, SU8 ThF-O2-50W/PFPE and SU8 ThF-O2-100W/PFPE) also show similar improvements in their frictional properties ( $\mu_i \sim 0.21/0.20/0.18$ ,  $\mu_s \sim 0.25/0.26/0.27$ , respectively), which are  $\sim 5$ – $7$  and  $\sim 2$ – $2.6$  times lower than those of the SU8 ThF surface, respectively. The modified surfaces show low values of coefficients of friction ( $\mu_i$  and  $\mu_s$ ) due to their semi-hydrophobic property, reduced contact areas and the lubrication effect of PFPE. Furthermore, the modified surfaces also show high wear durability ( $n > 100\,000$  cycles), which is  $> 1000$  times higher than that of the SU8 ThF surface. Interestingly, both the SU8 thick films coated with the nanolubricant (SU8 ThF/PFPE) and those modified by the two-step method performed effectively without failure for  $n > 100\,000$  cycles. In order to identify the surface modification for the best tribological performance, both these kinds of surfaces (SU8 ThF/PFPE and SU8 ThF-O2-25W/PFPE) were subjected to further tribological tests at loads higher than the applied normal load of 0.3 N, such as 0.8, 1 and 1.5 N.

Figure 6(b) shows the comparative tribological test results of the SU8 ThF/PFPE and SU8 ThF-O2-25W/PFPE surfaces at applied normal loads  $> 0.3$  N (0.8 N, 1 N and 1.5 N; Hertzian contact pressures  $\sim 88$  MPa, 95 MPa and 110 MPa, respectively). From the figure it can be seen that the SU8 ThF/PFPE surface shows lower wear durability with increase in the applied normal load. The surface fails at  $\sim 87\,700$  cycles at 0.8 N load, and at  $\sim 22\,000$  cycles at 1 N. Figures 7(b) and (c) show the optical micrographs of the worn surfaces of this test material tested at 0.8 N and 1 N, respectively, with considerable amount of wear debris on the wear tracks. Figures 7(f) and (g) show the surfaces of the counterface balls corresponding to the worn surfaces (b) and (c), with a large amount of material transferred to the ball surfaces. Compared with the SU8 ThF/PFPE, the SU8 ThF-O2-25W/PFPE surface shows excellent wear durability without any failure for  $n > 100\,000$  cycles at all the higher loads of 0.8, 1 and 1.5 N. Figures 7(d) and (h) show the optical micrographs of the SU8 ThF-O2-25W/PFPE surface and its counterface ball, taken after the test conducted at 1.5 N. From these images, it can be seen that the surface shows almost ‘no wear’ with very less material transfer, probably consisting of mobile PFPE molecules picked up from the surfaces during sliding. From the above observations, it is clear that the SU8 thick films modified by the two-step method are more robust than the SU8 thick films coated only with PFPE. The main reason for such an excellent wear durability of the SU8 thick films modified by the two-step method is attributed to the strong anchoring of PFPE molecules to the SU8 film surface, through chemical bonding. Hence, it is seen that by applying the two-step method to the SU8 thick film, the tribological performance of the film can be enhanced through the reduction in the frictional properties ( $\mu_i$  and  $\mu_s$ ) by  $\sim 5.8$ – $7$



**Figure 7.** Optical micrographs of worn surfaces: (a) SU8 ThF (at  $\sim 3000$  cycles, applied normal load: 0.3 N), (b) SU8 ThF/PFPE (at  $\sim 100\,000$  cycles, applied normal load: 0.8 N), (c) SU8 ThF/PFPE (at  $\sim 54\,000$  cycles, applied normal load: 1 N) and (d) SU8 ThF-O2-25W/PFPE (at  $\sim 100\,000$  cycles, applied normal load: 1.5 N). Images (e), (f), (g) and (h) are optical micrographs of the surfaces of counterface balls corresponding to the worn surfaces shown in (a), (b), (c) and (d), respectively. The scale bar is  $100\ \mu\text{m}$  in the images (a), (b) and (c), and is  $50\ \mu\text{m}$  in the remaining images.

times and by  $\sim 2.4$ – $2.6$  times, respectively, and simultaneously increasing the durability by  $> 1000$  times. It is noteworthy that the modified surfaces can perform effectively even at loads that are 5 times higher than the load at which the SU8 thick film fails within a short duration, thus indicating that the two-step surface modification method is a robust tribological solution for SU8-based miniaturized devices.

### 3.3. Further remarks

The two-step surface modification method is cost effective, as  $\text{O}_2$  plasma treatment is often used during MEMS/NEMS fabrication, and therefore can be easily integrated into the fabrication process without any additional cost. In addition, the coating of PFPE nanolubricant is done by dipping the surfaces in a solution of PFPE, and therefore neither additional expensive instruments/equipment nor any complex processes are involved. The two-step surface modification method is also time effective, as  $\text{O}_2$  plasma treatment is done for a time duration of 1 min, followed by the coating of PFPE nanolubricant for a time duration of 1 min. The entire two-step surface modification process takes only about 2 min of time and on its application, the Si and SU8 thick films that survive only for a very short duration ( $n < 100$  cycles, 30 s), perform effectively for  $n > 100\,000$  cycles ( $> 8$  h), even at higher applied normal loads. Moreover, the same method works effectively for both Si and SU8 thick films. The method can also work for any kind of structural material from which MEMS/NEMS are or can be made. Similarly to the present process of surface modification to Si, for any material, a thin SU8 film can be coated and treated by the two-step method, which would enhance the tribological performance of the material. Thus, the two-step method has all the features to be

a commercially viable tribological solution for MEMS/NEMS materials.

## 4. Conclusions

We have applied a two-step surface modification method to the two most important MEMS/NEMS structural materials, namely silicon and SU8 polymer, and have demonstrated significant enhancement in their tribological performance. On the application of the method to these materials, the initial coefficient of friction reduced by  $\sim 4$ – $7$  times and the steady-state coefficient of friction reduced by  $\sim 2.5$ – $3.5$  times. Simultaneously, the wear durability of both the materials increased by  $> 1000$  times. Factors such as semi-hydrophobicity/hydrophobicity, reduction in contact areas and the excellent lubrication property of PFPE contributed towards the significant reduction in their frictional properties, whereas the strong bonding of the nanolubricant molecules gave rise to their long-term wear durability. The two-step method is cost effective and time effective. The method can be readily and easily integrated into MEMS/NEMS fabrication processes.

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**References**

- [1] Kim S H, Asay D B and Dugger M T 2007 *Nanotoday* **2** 22
- [2] Henck S A 1997 *Tribol. Lett.* **3** 239
- [3] Maboudian R and Howe R T 1997 *J. Vac. Sci. Technol. B* **15** 1
- [4] Yoon E S, Singh R A, Oh H J and Kong H 2005 *Wear* **259** 1424
- [5] Bhushan B and Liu H 2001 *Phys. Rev. B* **63** 245412
- [6] Singh R A, Yoon E S, Han H G and Kong H 2007 *Wear* **262** 130
- [7] Bandorf R, Luthje H, Henke C, Wiebe J, Sick J H and Kuster R 2005 *Surf. Coat. Technol.* **200** 1777–82
- [8] Singh R A, Yoon E S, Kim H J, Kong H, Park S J and Lee K R 2006 *Surf. Coat. Technol.* **201** 4348
- [9] Yoon E S, Singh R A, Kong H, Kim B, Kim D H, Jeong H E and Suh K Y 2006 *Tribol. Lett.* **21** 31
- [10] Kustandi T S, Choo J H, Low H Y and Sinha S K 2010 *J. Phys. D: Appl. Phys.* **43** 015301
- [11] Singh R A, Pham D C, Kim J and Yoon E S 2009 *Appl. Surf. Sci.* **255** 4821
- [12] Asay D B, Dugger M T, Ohlhausen J A and Kim S H 2008 *Langmuir* **24** 155
- [13] Abgrall P, Conedera V, Camon H, Gue A M and Nguyen N T 2007 *Electrophoresis* **28** 4539
- [14] Seidemann V, Rabe J, Feldmann M and Buttgenbach S 2002 *Microsyst. Technol.* **8** 348
- [15] Foulds I G and Parameswaran M 2006 *J. Micromech. Microeng.* **16** 2109
- [16] Lorenz H, Despont M, Vettiger P and Renaud P 1998 *Microsyst. Technol.* **4** 143
- [17] Jiguet S, Judelewicz M, Mischler S, Hofmann H, Bertsch A and Renaud P 2006 *Surf. Coat. Technol.* **201** 2289
- [18] Jiguet S, Judelewicz M, Mischler S, Bertsch A and Renaud P 2006 *Microelectron. Eng.* **83** 1273
- [19] [www.microchem.com](http://www.microchem.com)
- [20] Bhushan B 1998 *Principles and Applications of Tribology* (New York: Wiley)
- [21] Walther F, Davydovskaya P, Zurcher S, Kaiser M, Herberg H, Gigler A M and Stark R W 2007 *J. Micromech. Microeng.* **17** 524
- [22] Satyanarayana N and Sinha S K 2005 *J. Phys. D: Appl. Phys.* **38** 3512
- [23] Walther F, Heckl W M and Stark R W 2008 *Appl. Surf. Sci.* **254** 7290
- [24] Satyanarayana N, Sinha S K and Ong B H 2006 *Sensors Actuators A* **128** 98
- [25] Satyanarayana N, Gosvami N N, Sinha S K and Srinivasan M P 2007 *Phil. Mag.* **87** 3209
- [26] Satyanarayana N, Lau H K and Sinha S K 2008 *Appl. Phys. Lett.* **93** 261906
- [27] Bhushan B 1996 *Tribology and Mechanics of Magnetic Storage Devices* (New York: Springer)
- [28] Wu C S and Liao H T 2007 *Polymer* **48** 4449
- [29] Kumeta K, Nagashima I, Matsui S and Mizoguchi K 2003 *J. Appl. Polym. Sci.* **90** 2420
- [30] Minn M and Sinha S K 2008 *Surf. Coat. Technol.* **202** 3698