APPLIED PHYSICS LETTERS **93**, 261906 (2008)

Nanolubrication of poly(methyl methacrylate) films on Si for microelectromechanical systems applications

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(Received 8 July 2008; accepted 5 December 2008; published online 31 December 2008)

Polymers, such as poly(methyl methacrylate) (PMMA), are important structural materials for microsystems because of their excellent mechanical properties; however, they suffer from severe problems of adhesion, friction, and wear [B. Bhushan, J. N. Israelachvili, and U. Landman, Nature (London) **374**, 607 (1995)]. We report a simple process of O_2 plasma treatment on a PMMA film, followed by overcoating with an ultrathin layer of perfluoropolyether (PFPE) which improved tribological performance of the film. O_2 plasma on PMMA film has formed unique wavy nanotextured surface and increased the hardness and the elastic modulus of the film, which, together with the nanolurbication by PFPE, has increased the wear life of PMMA film by more than five orders of magnitude. © *2008 American Institute of Physics*. [DOI: 10.1063/1.3062847]

Microelectromechanical systems (MEMS) market is poised to grow from less than U.S.$8 billion presently to U.S.$14 billion by 2012;[1] however, there are many engineering challenges related to the design and reliability of these micromechanical devices that may restrict this expected market growth. Some of the major reliability issues in MEMS are the tribological problems, i.e., high friction, adhesion, and wear. Many of the current designs of MEMS do not include rubbing surfaces in order to avoid these tribological problems; however, this poses limitations in the applicability and performance maximizations of MEMS. Therefore, solutions to the above problems are essential for the development of MEMS products with greater functionality and for the realization of their commercial potentials. For MEMS, surface properties are very crucial due to the high surface-area-to-volume ratio of its microcomponents. Furthermore, it is important that the surface shows acceptably low friction and low or "zero" wear for the entire life cycles of the machine which may involve millions of cycles of operation. poly(methyl methacrylate) (PMMA) is one of the structural materials used for the fabrication of MEMS.[2] Another popular material is Si. Similar to Si, PMMA is a poor tribological material and shows high friction, adhesion, and wear in its pristine form.[3] Hence, to increase the reliability of MEMS components, the tribological properties of PMMA have to be improved. Only limited research has been conducted on improving the tribological properties of PMMA, e.g., on reducing the coefficient of friction.[3] There is no solution yet on improving the wear durability of PMMA surfaces. So far, the research has been conducted to characterize and understand the adhesive force, frictional force, and wear of PMMA.[4]

In this letter, we discuss a method of improving the tribological properties of PMMA film on Si. The method involves a combination of O_2 plasma treatment of PMMA film, followed by overcoating the film with an ultrathin layer of PFPE onto O_2 plasma-treated PMMA film (herewith denoted as O_2-PMMA film). The resulting film has shown a greater reduction in friction coefficient and exceptional improvement in wear life when compared with those of pristine PMMA film. PMMA film of 400 nm thickness was formed on Si (100) surface from a solution of 4 wt % PMMA (with molecular weight of 950 000) in anisole (solvent: methoxybenzene) using spin coating at 1000 rpm for 1 min, followed by post-heating at a temperature of 180 °C for 1 min. O_2 plasma treatment of PMMA film was conducted using reactive ion etcher at a power of 60 W, gas flow of 100 SCCM (SCCM denotes cubic centimeter per minute at STP), and at a chamber pressure of 150 Pa for 45 s. In the case of plasma cleaning, the operating conditions, such as plasma treatment power, air flow, oxygen pressure, and etching time greatly, affect the surface condition.[5] In the present work, only the time of the plasma exposure was optimized while keeping all the other parameters fixed. Perfluoropolyether (PFPE) coating onto unmodified and modified PMMA surfaces was carried out using a custom-built dip-coating machine from a solution of 0.2 wt % Z-dol PFPE (with molecular weight of 4000) dissolved in H-Galden ZV 60 (hydrofluoropolyether solvent).[6] The PFPE film formed with the above depositional conditions shows a film thickness of 10–20 Å.[7,8] Details of the water contact angle measurement, atomic force microscope (AFM) imaging, nanoindentation measurements, and microtribological tests can be obtained from Refs. 6 and 9.

Table I shows the water contact angle results of all surfaces studied. The observed changes in the wettability from one surface to another surface support the differences in the chemical and/or physical changes due to that particular modification. O_2 plasma treatment has made the surface of PMMA film hydrophilic. It is noted that the water contact angle values for PFPE coated pristine PMMA film and PFPE coated O_2-PMMA film are approximately similar. The water contact angle values of PMMA film with and without O_2 plasma treatment are consistent with the literature results.[10,11]

Figure 1 shows the AFM images of various surfaces studied in the present work. O_2 plasma treatment of PMMA film has generated a unique texturing consisting of islands to an otherwise smooth surface and increased the roughness of the surface. PFPE overcoating onto unmodified PMMA film has generated a flat surface, whereas that onto O_2-PMMA film has shown a nanotextured surface with much higher roughness (~7.95 nm) than that of the O_2-PMMA surface. After overcoating PFPE onto O_2-PMMA surface, the number

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TABLE I. Water contact angle, roughness, elastic modulus, hardness, coefficient of friction, and wear life for all surfaces studied in the present work. Coefficient of friction and wear life data were obtained in a sliding test against 4 mm diameter Si_3N_4 ball at a contact pressure of 612 MPa and a sliding velocity of 0.042 m/s.

Sample	Water contact angle (deg)	Roughness (nm)	Elastic modulus (GPa)	Hardness (GPa)	Coefficient of friction	Wear life (No. of cycles)
Bare Si	12.0	0.25	⋯	⋯	0.48	Few cycles
Si/PMMA	72.5	0.39	8.28	0.31	~0.60	Few cycles
Si/PMMA-O_2 plasma	45.0	0.92	12.96	0.46	0.42	Few cycles
Si/PMMA/PFPE	80.3	1.08	8.76	0.38	0.15	~150
Si/PMMA-O_2 plasma/PFPE	78.4	7.95	8.23	0.37	0.10	>100 000

of islands is reduced, whereas the dimensions, the total height and the base width of the islands, have increased approximately seven to eight and four to five times, respectively. We measured the attack angles of many of the asperity-looking island peaks for both Si/PMMA-O_2 and Si/PMMA-O_2/PFPE surfaces and found them to be in the ranges of 7.5°–14° and 13°–27°, respectively. The attack angles show that the nanotextured islands became slightly sharper after overcoating PFPE onto O_2-PMMA. The geometry of the islands influences the frictional force and affects the wear process. The physical as well as chemical interactions between the PMMA molecules (modified and unmodified) and PFPE molecules have led to the differences in the topography. When PFPE is coated onto O_2-PMMA film, the surface texture profile is similar in appearance to that of O_2-PMMA except that the sharpness (or the attack angle) and the dimensions (total height and the width of the base) of the island increase due to the accumulation of the PFPE molecules on the previous texture.

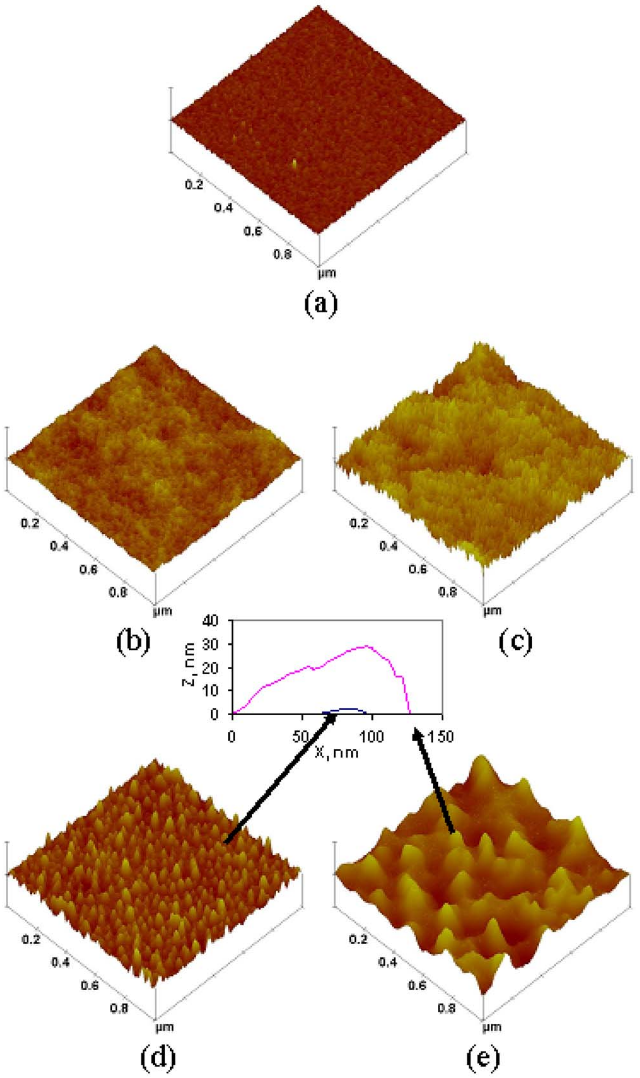

FIG. 1. (Color online) AFM topography images of (a) bare Si, (b) Si/PMMA, (c) Si/PMMA/PFPE, (d) Si/PMMA-O_2 plasma, and (e) Si/PMMA-O_2 plasma/PFPE. The scan size is 1×1 μm^2 and the vertical scale is 10 nm in all samples except in (e) where the vertical scale is 50 nm. The plot at the center compares the line scan dimensions of the islands formed before (blue line) and after (pink line) PFPE coating on O_2-PMMA surface.

Nanoindentation tests were carried out using continuous stiffness measurement module. O_2-PMMA has shown higher elastic modulus (by ~56.5%) and hardness (by ~48.4%) when compared to the corresponding values for pristine PMMA film. These results are in good agreement with the literature values.[12] The reasons for this behavior is explained as an increase in the cross-linking of polymer molecular chains because of the generation of chemical groups, which eventually increase the interaction forces between the PMMA molecules. As a result, the molecular packing improves and hence the mechanical properties are improved correspondingly. PFPE coating onto pristine PMMA film has shown similar or slightly improved elastic modulus and hardness values when compared with those of pristine PMMA, whereas PFPE overcoating onto O_2-PMMA has shown a decrease in elastic modulus (by ~36.5%) and hardness (by ~19.6%) when compared to those corresponding to O_2-PMMA. Because of these opposite trends, the nanomechanical properties of Si/PMMA/PFPE and Si/PMMA-O_2/PFPE samples are almost identical.

Ball-on-disk sliding tests have shown that both pristine and O_2-PMMA films failed instantly after the start of the tests, whereas PFPE overcoated pristine PMMA film has shown a wear life of ~150 cycles. PFPE overcoating onto O_2-PMMA film has greatly increased the wear life from few cycles to more than 100 000 cycles (Fig. 2). There was no generation of wear debris for Si/PMMA-O_2/PFPE case until 100 000 cycles of sliding at a normal load of 0.3 N (Hertzian contact pressure=612 MPa) and a sliding speed of 200 rpm (0.042 m/s) (Fig. 3). Even after sliding for 100 000 cycles, the coefficient of friction remained less than 0.3 with the obvious sign of "zero wear." AFM imaging inside the wear track of Si/O_2-PMMA/PFPE has shown very smooth surface with some signs of sliding marks [Fig. 3(d)]

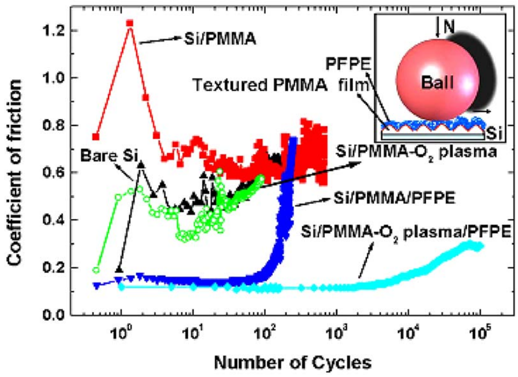

FIG. 2. (Color online) Coefficient of friction vs number of cycles for a typical run for all the surfaces studied in the present work. The normal load and sliding velocities used are 30 g and 0.042 m s^{-1}, respectively. The inset shows a graphical model of the contact between the ball and PFPE coated O$_2$-PMMA islands (the drawing is not to scale). At least five samples were tested for each surface modification and the wear life data were found to be consistent.

and strongly supports the exceptionally high durability of Si/O$_2$-PMMA/PFPE.

A very high wear durability of the presently demonstrated film with the intermediate O$_2$ plasma treatment is attributed to the beneficial effect from both O$_2$ plasma treatment of PMMA film and overcoating of PFPE. It may be noted that, when applied alone, either PFPE overcoated pristine PMMA film or O$_2$ plasma treated PMMA film did not show any beneficial effect on improving the wear life. This is despite the fact that O$_2$ plasma treatment improved the surface nanomechanical properties such as hardness and elastic modulus. O$_2$ plasma treatment usually generates chemical groups such as carboxylic, carbonyl, and hydroxyl groups.[13] The carboxylic and O$_2$-functional groups are very reactive toward end-hydroxyl groups of PFPE molecules and hence they contribute to the increased chemical interactions between the PFPE molecules and PMMA molecules which help in improving the wear life. Further, the resulting nanotexture after O$_2$ plasma treatment has reduced the effective contact area and hence led to a reduction in the coefficient of friction. The role of PFPE is very crucial as PFPE has linear fluorinated molecular structure which is ideal for lubricity. The PFPE coating onto pristine PMMA film has shown very smooth and flat surface without any island structure. Such structure usually shows higher contact areas and hence higher friction. As there are no (or negligibly small) chemical interactions between PFPE and PMMA molecules, PFPE molecules can be relatively easily displaced out from the contact region during sliding showing very low wear life.

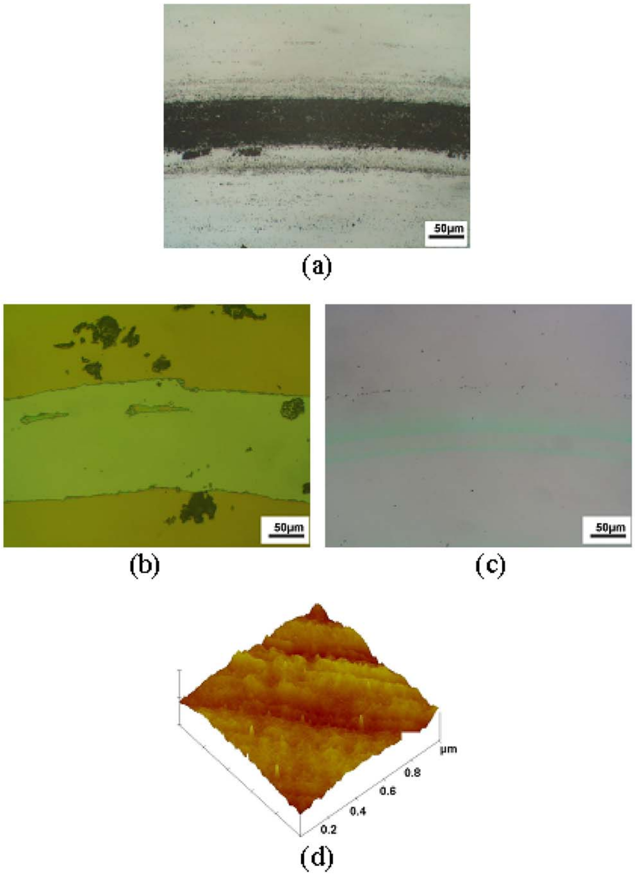

FIG. 3. (Color online) Optical images of wear tracks for (a) bare Si after 200 cycles of sliding, (b) Si/PMMA/PFPE after 250 cycles of sliding, and (c) Si/PMMA-O$_2$ plasma/PFPE after 100 000 cycles of sliding. The normal load and sliding velocity used are 30 g and 0.042 m s^{-1}, respectively. (d) AFM image inside the wear track of the sample shown in (c) with the scan size of 1×1 μm^2 and the vertical scale of 10 nm.

Thus, the present results show combined beneficial effects of nanotexturing by O$_2$ plasma treatment and nanolubrication by PFPE on hydrophilic O$_2$-PMMA surface in achieving extremely high wear life of a tribologically poor material. The present method of O$_2$ plasma treatment and PFPE overcoating can be easily applied onto any polymer surface, and similar improvement in the wear durability is expected. Therefore, this method can find many applications in areas such as biology, biomedical, nanotechnology, and microelectronics, where low adhesion, low friction, and high wear durability are essential.

This work was supported by the NUS under Research Grant No. R-265-000-248-112.

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