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TRIBOLOGY OF PFPE OVERCOATED SELF-ASSEMBLED MONOLAYERS DEPOSITED ON SILICON SURFACE: EFFECT OF THERMAL TREATMENT

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ABSTRACT

Effect of thermal treatment on the friction and wear of monomolecular layers of SAMs (Self-assembled monolayers) overcoated with PFPE was studied using ball-on-disk tribometer. Two SAMs, Octadecyltrichlorosilane (OTS) and 3-aminopropyltrimethoxysilane (APTMS) were formed on the Si substrate by self-assembly followed by dip-coating with perfluoropolyether (PFPE). Modified Si samples are thermally treated at 150 °C under vacuum for 2h. The physical and chemical properties of modified samples, before and after thermal treatment, are analyzed using contact angle measurements, X-ray photoelectron spectroscopy (XPS). Tribological properties are evaluated using Universal Micro Tribometer (UMT). A Si₃N₄ ball of 4mm diameter is used as the counterface. Thermal treatment of the PFPE coated SAMs and Si surface reduced the coefficient of friction to slightly lower values in all cases. Thermal treatment has shown slight increase in wear life in the case of PFPE coated APTMS SAM surfaces whereas it decreased the wear life in the case of PFPE coated OTS SAM and Si surfaces. The exact reasons for this behavior are not clear at present, but it is being speculated that thermal treatment effects the extent of bonding between the surface groups of PFPE and SAMs and mobile characteristics of the PFPE, which finally influence the wear durability characteristics. Therefore, the differences in the wear durability characteristics are analyzed using changes in the surface energies and the amount of strongly adsorbed PFPE, as a result of thermal treatment.

INTRODUCTION

Micro-miniaturization is a current trend in the development of electromechanical devices known as microelectromechanical systems (MEMS). The performance of MEMS components is limited because of their large surface area-to-volume ratios. Moreover contact related adhesion and friction phenomena become stringent problems for these systems. Hence, ultra-thin organic molecular layers have been proposed as the lubricants for Si based MEMS systems. Alkyl silane SAMs have been extensively studied. They can reduce coefficient of friction,

stiction and wear when they are deposited onto the Si substrate. 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. 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. We found that there was remarkable increase in wear resistance when PFPE is coated as a top layer onto the reactive SAM surfaces and little improvement on non-polar SAM coated Si surfaces [1]. In the present study we investigated the effect of thermal treatment on these PFPE coated SAM surfaces.

EXPERIMENTAL PROCEDURE

The detailed procedure for the deposition of SAMs, dip-coating of PFPE, properties of SAM materials and PFPE are reported in a previous publication [1]. PFPE contains two hydroxyl groups, one each at the end of its linear chain. OTS SAM has non-polar methyl terminal groups whereas APTMS SAM molecules contain polar amine terminal groups. The PFPE coated SAMs and Si surfaces are heated under vacuum at 150 °C for 2h and then cooled to room temperature in the furnace itself.

A water droplet of 0.5 to 1 µl was used for contact angle measurements using VCA optima contact angle system. The chemical state of the sample surface, before and after thermal treatment and after rinsing of PFPE with the H-Galden solvent, was studied by XPS. Friction and wear tests were carried out on UMT-2, using ball-on-disk mode, by employing a Si₃N₄ ball of 4mm diameter and at a normal load of 50mN (approximate Hertzian contact pressure of 330MPa). 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. The wear life data have been obtained on at least three different samples and an average value is reported in the present article.

RESULTS AND DISCUSSION

Thermal treatment after PFPE coating onto SAMs and bare Si has shown higher water contact angles. In the case of SAM coated Si surfaces, there is little/negligible difference in the water contact angles after PFPE coating with and without thermal treatment. Therefore, thermal treatment did not show any effect on the surface energy of PFPE coated SAM surfaces. In contrast there was a considerable increase in water contact angle from 67° to 112° in case of PFPE coated Si surface after thermal treatment (Fig.1). The heat treatment procedure of the attached PFPE film on Si surface results in significant increase of the molecular weight of the polymer through evaporation of lower molecular weight fractions as reported by J. Ruhe et al [2]. 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 the Si surface. The same phenomenon might have happened in case of the PFPE coated SAM surfaces also, but it has not been reflected in the water contact angle values, because the water contact angle values already reached the saturated values of the hydrocarbon or fluorocarbon films, even before the thermal treatment.

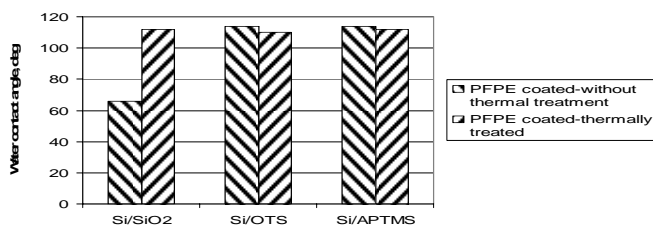


Fig.1. Water contact angles of PFPE coated SAMs and Si surfaces with and without thermal treatment.

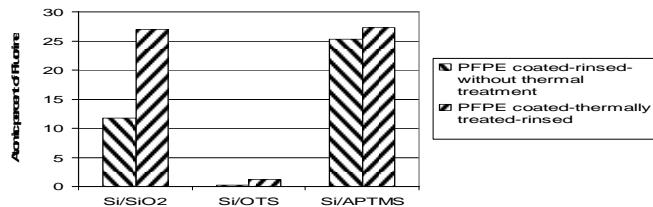


Fig.2. Atomic percent of fluorine of PFPE coated SAMs and Si after rinsing with and without the thermal treatment.

The atomic percent of fluorine were obtained from the XPS measurements for PFPE coated SAMs and Si, after rinsing, with and without thermal treatment. There is an increase in percentage of fluorine, after thermal treatment and rinsing, in case of both PFPE coated SAMs and Si surfaces (Fig.2). Hence we can conclude that thermal treatment aids in enhancing the bonding of the PFPE. More amount of PFPE is bonded in case of the PFPE coated Si, after thermal treatment, than PFPE coated SAMs. We believe that these differences in the bonding of the PFPE influence the final tribological properties.

There was a slight decrease (but not significant) in the coefficient of friction after thermal treatment of the PFPE coated SAMs and Si surfaces. This can be inferred to the increase in the density of the polymer molecules after thermal treatment.

Thermal treatment has shown good improvement in wear resistance of PFPE coated APTMS SAM. There was about 30% improvement in wear life after thermal treatment.

Surprisingly, thermal treatment on PFPE coated OTS SAM surface has shown lower wear life than just OTS modified Si surfaces. Despite same values of the water contact angle for the case of PFPE modified APTMS SAM and Si surface after thermal treatment, there was a little decrease in wear life after thermal treatment of PFPE modified Si surface. The exact reasons for this conflicting behavior are not very clear currently and a detailed study is in progress. XPS results have shown the differences in the bonded portions of PFPE coated APTMS SAM and Si, after thermal treatment, which might have been the reason for the differences in the wear behavior. One more interesting result that can be observed from the wear life graph shown in Fig.4 is, the scatter in the wear life data has been reduced after thermal treatment. This can be attributed to the removal of the lower melting point organic contaminants.

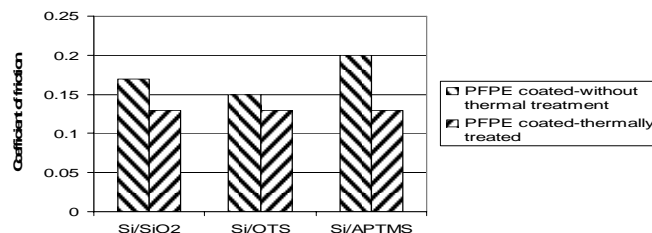


Fig.3. Coefficients of friction of PFPE coated surfaces before and after thermal treatment.

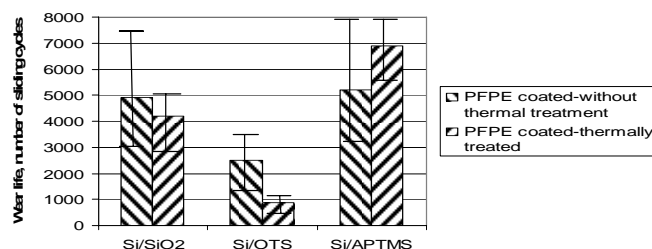


Fig.4. Wear life of PFPE coated surfaces before and after thermal treatment

In conclusion, thermal treatment of the PFPE coated SAMs and Si surface has shown mixed results as far as the wear durability characteristics are concerned. There was good improvement in the wear durability in the case of thermally treated PFPE coated APTMS SAM. Therefore, PFPE coated APTMS SAM coupled with thermal treatment can find applications in MEMS components.

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REFERENCES

1. N.Satyanarayana and S.K.Sinha, "Tribology of PFPE overcoated self-assembled monolayers deposited on Si surface", submitted to Journal of Physics D: Applied Physics, 2005.
2. J.Ruhe, G.Blackman, V.J.Novotny, T.Clarke, G.B.Street and S.Kuan, "Terminal attachment of Perfluorinated Polymers to Solid Surfaces", Journal of Applied Polymer Science, 53 (1994) 825-836.