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Effect of Air–Plasma Pre-treatment of Si Substrate on Adhesion Strength and Tribological Properties of a UHMWPE Film

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Abstract

Ultra High Molecular Weight Polyethylene (UHMWPE) film is dip coated onto piranha and air–plasma treated silicon substrates, to study the effect of surface pre-treatment on the adhesion strength and the tribological properties of the film. After the pre-treatment, water contact angle measurements were conducted and the surface free energy of the Si substrate was calculated. It is observed that the air–plasma pre-treatment reduced the water contact angle (4.3^{O}) considerably when compared to that of the piranha pre-treatment (21.3^{O}), which resulted in an increase of the surface free energy of the Si substrate. Scratch tests were conducted for studying the adhesion property of UHMWPE films coated onto Si substrate. It was found that the plasma pre-treatment enhanced adhesion between the UHMWPE film and the Si substrate by more than two times when compared to the piranha pre-treatment. Wear tests were conducted to study the effects of pre-treatments on the tribological properties of the UHMWPE film. UHMWPE film coated onto plasma pre-treated Si showed a wear life of about 50 000 cycles (25 times higher) as compared to that of 2000 cycles when it was coated onto piranha pre-treated Si, tested at a normal load of 1 N and a rotational speed of 200 rpm.

Keywords
Air–plasma treatment, UHMWPE film, wear durability of Si

1. Introduction

Silicon (Si) is one of the widely used materials in microelectromechanical systems (MEMS) and microsystems. However, bare Si, without proper surface modification, exhibits high friction, adhesion and wear [1]. Several types of ultra-thin films have been proposed recently for improving the tribological properties of Si and MEMS made from Si [2–6]. One important category of these films are the polymer coatings, which have found their way in various tribological applications due to their excellent self-lubricating properties, low production cost, ease of coating procedures, and corrosion resistance [7–9]. However, despite their self-lubrication property, these polymer coatings usually suffer from poor adhesion to the substrate, thus resulting in low wear life [10, 11]. Various pre-treatment processes, such as piranha treatment, have been used to enhance the adhesion property of the Si substrate and the polymer film. Piranha treatment, besides using harmful chemicals such as hydrogen peroxide and sulphuric acid, is a laborious process involving long reaction time (approximately 2 h [2]).

Lately, the potential of air–plasma, as an effective pre-treatment process for improving the adhesion strength between the polymer films and the substrates, is being explored extensively due to its various advantages such as no use of harmful chemicals, ease of handling, ease of adaptability to industrial applications and ease of treating intricate geometries [12, 13].

UHMWPE was selected as the polymer coating for its excellent wear resistance and self-lubricating properties as well as for exploring a way to improve the tribological properties of polymer films by suitable environmental-friendly pretreatment of the substrate prior to the polymer coating [11].

Thus, the main objective of this study was to investigate and compare the effects of air–plasma and piranha pre-treatments of the Si substrate on the adhesion strength and the tribological properties of the UHMWPE film coated onto the Si surfaces. Scratch test was conducted for the adhesion study whereas ball-on-disk test was employed for the tribological evaluation of the films. Various surface characterization techniques such as X-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM) and field-emission scanning electron microscopy (FESEM) were used to study the surfaces.

2. Experimental Procedures

2.1. Materials

Polished single crystal silicon (100) wafers were used as the substrate. The Si wafers were cut into pieces of approximately 2 cm × 2 cm and then used for the surface modification. UHMWPE polymer powder (Grade: GUR X 143) used for coating the specimens was supplied by Ticona Engineering Polymers, Germany and was procured from a local Singapore supplier ("melt index MFR 190/15" = 1.8 ± 0.5 g⁄10 min; bulk density = 0.33 ± 0.03 g/cm3; average particle size = 20 ± 5 μm). Decahydronaphthalin (decalin) was used as the solvent to dissolve the polymer powder prior to dip-coating.

2.2. Pre-treatment Procedures

In the present study, the Si substrate was subjected to two different pre-treatments, piranha and air–plasma pre-treatments, prior to the UHMWPE coating. The pretreatment procedures were as follows.

2.2.1. Piranha Pre-treatment

Si samples were ultrasonically cleaned successively using soapy water and distilled water followed by rinsing with acetone for 10 min. The samples were then hydroxylated by

immersing in a piranha solution, a mixture of 7 : 3 (v/v) 98% H_2SO_4 and 30% H_2O_2 at 60–70◦C for 50 min. After piranha treatment, the samples were thoroughly rinsed successively with distilled water and acetone. The total time for treating the Si samples by piranha treatment was approximately 90 min. Further details can be found in [8].

2.2.2. Air–Plasma Pre-treatment

Si samples were cleaned with distilled water and acetone successively in an ultrasonic bath prior to drying using nitrogen gas. The samples were then air–plasma treated using a Harrick Plasma Cleaner/Steriliser. The sample surface was exposed to plasma under vacuum for approximately 5 min using an RF power of 30W. Care was taken not to expose the surface to any further contamination and thus it was immediately processed for the dip coating. The total time for treating the Si samples by air–plasma treatment was approximately 20 min.

2.3. Coating Procedure

UHMWPE polymer in powder form was dissolved in decalin by heating the solution to 80 ^{O} C for 30 min followed by another heating sequence to 160 ^{O} C for 30 min. Magnetic stirrers were used for uniform distribution of heat in the solution and for speeding up the dissolution process. The solution was used once it turned from milky to transparent appearance indicating a complete dissolution. The specimens were dip-coated using a custom-built dip-coating machine which could submerge and withdraw the sample at a speed of 2.1 mm/s [8, 11, 14, 15]. The samples were held in the polymer–decalin solution for 30 s in submerged condition prior to withdrawal.

The coated samples were dried in air for 60 s and then post-heat-treated in a hot oven at 120 ^{O} C for about 20 h. After the post-heat-treatment, the samples were cooled slowly to room temperature in an oven and stored carefully in a desiccators before proceeding to tribological testing. Further details can be found in [2].

2.4. Surface Characterization and Analysis

A VCA Optima Contact Angle System was used for the measurement of contact angles with three different liquids: de-ionized water, ethylene glycol, and hexadecane. A 0.5 μl droplet was used for the contact angle measurement. A total of five independent measurements were performed randomly at different locations on the samples and an average value was taken for each sample. The measurement error was within ±3◦.

An atomic force microscope (Dimension 3000 AFM, Digital Instruments, USA) was used to study the surface topography of the Si bare surface after appropriate pre-treatment, and after coated with UHMWPE film. A silicon tip was used for scanning and images were collected in air in the tapping mode.

A Kratos Analytical AXIS HSi spectrometer (XPS) was used for the surface analysis. XPS (Al Kα source) imaging was performed with an X-ray source (1486.6 eV photons) at a constant dwell time of 100 ms and a pass energy of 40 eV. The core level signals were obtained at a photoelectron take-off angle of 90 ^{O} (with respect to the sample surface). All binding energies (BEs) were referenced to the C1s hydrocarbon peak at 284.6 eV. In peak synthesis, 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 using XPS Peak Fitting Program, XPSPEAK41.

2.5. Thickness Measurement

Thickness of the polymer film on Si surface was measured by observing the cross section of the sample (after film coating) using field emission scanning electron microscopy

(FESEM, Hitachi S4300). The coated samples were cut using a diamond scriber and a plier and mounted with their cross sections horizontal. Ten independent measurements were taken on each sample and the average value was reported. The thickness variation was within ±1 μm. Before observing the samples under FESEM, gold was deposited on the films at 10 mA for 40 s using a JEOL, JFC-1200 Fine Coater.

2.6. Surface Free Energy Calculations

Surface free energy calculations were carried out using the acid–base approach [16]. This method requires measurement of contact angles on the substrate using three different, completely characterized liquids, two of which have to be polar and the third apolar. The dispersion component of the surface tension (γ_1^d), the acid component of the surface tension (γ_1^+) and the base component of the surface tension (γ_1^-) of all the liquids were obtained from literature. The measured contact angle values are substituted in the following equation [16]:

$$0.5(1+\cos\theta)\gamma_1 = \left(\gamma_s^d \gamma_1^d\right)^{1/2} + \left(\gamma_s^- \gamma_1^+\right)^{1/2} + \left(\gamma_s^+ \gamma_1^-\right)^{1/2},$$

where γ_s^d, γ_s^+ and γ_s^- refer to the dispersion, acid, and base components of the surface tension (surface free energy) of the solid substrate, respectively. These unknowns are calculated by solving the three equations resulting from the substitution of the contact angle values of the three liquids. The total surface free energy of the solid substrate is given by [16]:

$$\gamma_s = \gamma_s^d + 2\left(\gamma_s^+ \gamma_s^-\right)^{1/2}.$$

2.7. Scratch Test

Scratch tests were carried out on a custom-built scratch tester using a conical diamond tip of radius 2 μm. The length of the scratch and the traverse velocity of the tip were kept constant for each scratch as 10 mm and 0.1 mm/s, respectively. Normal load was also kept constant for each scratch. However, the normal load was varied from 10 mN to 100 mN with an increment of 10 mN for every successive scratch. After the test, the scratches were characterized using FESEM/EDS (energy dispersive spectroscopy) technique to ascertain the critical load defined as the load at which the polymer film showed signs of failure which was characterized by the peeling-off or ploughing mechanism and the appearance of Si peaks (because of exposed substrate) in the EDS spectrum. Before observing the scratches under FESEM (Field Emission SEM), gold was deposited on the films at 10 mA for 40 s using a JEOL, JFC-1200 Fine Coater.

2.8. Friction and Wear Tests

Ball-on-disk wear tests were carried out on a UMT-2 equipment (Universal Micro Tribometer, CETR Inc., USA) under dry conditions using ball-on-disk mode. A silicon nitride ball of _4 mm with a root mean square (RMS) surface roughness of 5 nm (as provided by the supplier) was used as the counterface material. The ball was thoroughly cleaned with acetone before each test. The wear track radius was fixed at 2 mm for all the tests. In this study, wear life of the thin film is defined as the number of cycles when the coefficient of friction exceeds 0.3 or when continuous large fluctuations are observed in

the coefficient of friction data (indicative of film failure), whichever happens first [17]. The wear tests were carried out at a normal load of 1 N and a rotational speed of 200 rpm corresponding to a sliding velocity of 0.042 m/s. At least ten repetitions were carried out and average values were calculated to report the final friction and wear life data. Tests were carried out in a clean booth environment (class 100) at a temperature of 25±2◦C and a relative humidity of 55 ± 5%. After every test, the counterface and sample surfaces were examined under an optical microscope for investigating the wear mechanisms. At least 10 samples from 3 different batches were tested and an average value of wear life was reported.

3. Results and Discussion

3.1. Effect of Pre-treatment on the Wettability and the Surface Free Energy of the Si Substrates

Table 1 shows the contact angles measured with DI-water, ethylene glycol and hexadecane, and surface free energy of the untreated Si, piranha treated Si and air–plasma treated Si. It is observed that the Si surface which was subjected to air– plasma pre-treatment exhibited lowest contact angles leading to an increase in the surface free energy when compared to that of the piranha treated and untreated Si samples which exhibited lower surface free energies.

Figure 1 shows AFM topographical images for untreated Si, piranha-treated Si and plasma-treated Si, and the corresponding roughness values are reported in Table 1. Both the air–plasma and the piranha pre-treatments were effective in reducing the roughness of the Si surface which might be because of the removal of the organic and/or inorganic contaminants.

Table 1.
Contact angles measured with DI-water, ethylene glycol and hexadecane, for various surface pre-treatments of Si and corresponding surface free energy values. The table also lists the RMS (root mean square) roughness of untreated Si and after two different treatment methods used

Surface	DI-water (°)	Ethylene glycol (°)	Hexadecane (°)	Surface free energy (mJ/m^2)	RMS roughness (nm)
Si-untreated	38.4	21.6	6.1	44.7	0.53
Si-piranha treated	21.3	17.8	4.8	45.4	0.25
Si-plasma treated	4.3	3.9	4.7	47.3	0.29

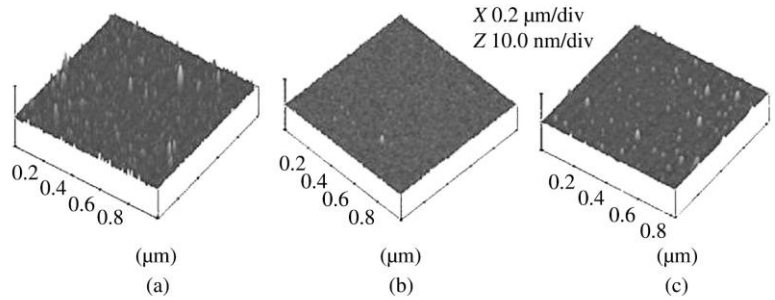

Figure 1. AFM topography images for (a) Si-untreated; (b) Si-piranha treated and (c) Si-plasma treated. The scan area used is 1 μm × 1 μm and the vertical scale is 10 nm.

Figure 2 shows the FESEM/AFM morphology of UHMWPE films on piranhatreated and plasma-treated Si. The morphology of polymer film is almost the same in both cases and we can conclude that the pre-treatment of Si does not have any effect on the morphology of UHMWPE film coated onto Si. It is also observed that the pre-treatment of the Si surface does not affect the thickness of the UHMWPE film. The film thicknesses were calculated as explained earlier and were found to be ∼16.6 μm and ∼15.2 μm for the air–plasma pre-treatment and piranha pre-treatment, respectively. Further, Si-plasma/UHMWPE showed a water contact angle of 117◦ whereas Si-piranha/UHMWPE showed a water contact angle of 108^{O}.

3.2. XPS Analysis of the Si Surface

XPS was used to study the chemical state of the Si surfaces after the plasma and piranha treatments. Table 2 shows the atomic percent of C and O on untreated, piranha- and plasma-treated Si surfaces obtained from XPS analysis. It can be observed from Table 2 that after the plasma treatment there is a decrease in the atomic percent of C and an increase in the atomic percent of O when compared to untreated and piranha-treated Si surfaces. The core level spectra (after curve fitting) of C1s and O1s of piranha- and plasma-treated Si surfaces are shown in Figs 3 and 4, respectively. The curve-fit data with peak assignments are shown in Table 3. The C1s spectra for both piranha- and plasma-treated Si surfaces contain peak components corresponding to C–C/C–H at 284.6 eV, C–O at 286.2 eV and C=O at 289 eV [18]. However, the peak area is less in the case of plasma-treated Si than that corresponding to the untreated and piranha-treated Si for all the three peaks suggesting that the air–plasma treatment is more effective in removing the organic contaminants from the Si surface.

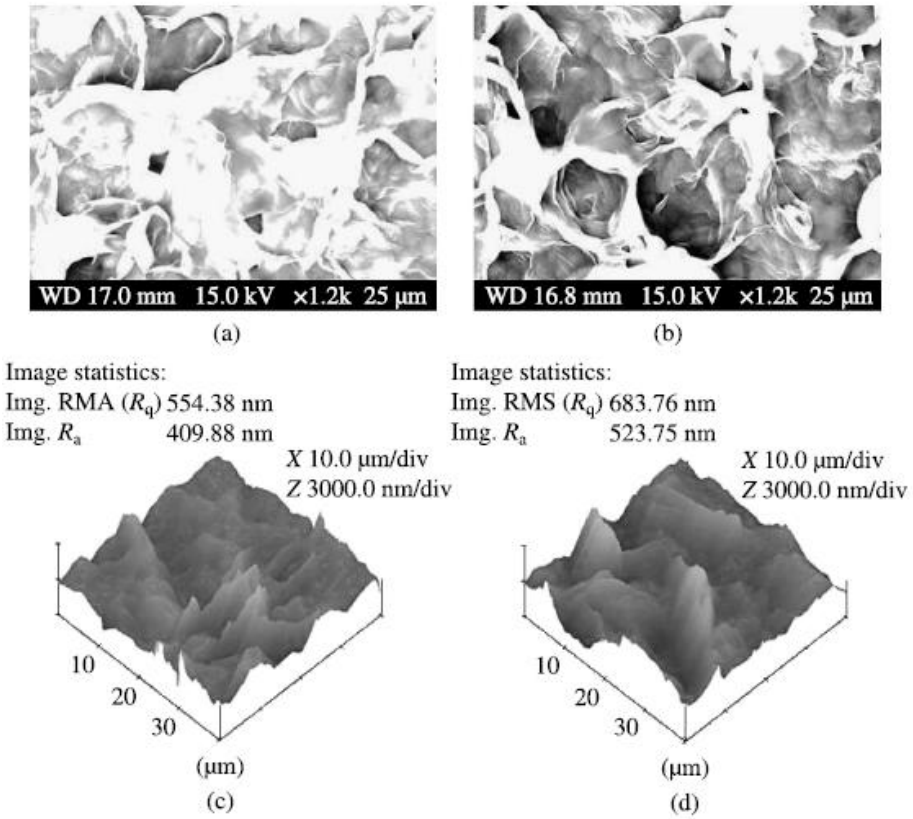

Figure 2. FESEM/AFM morphology of (a), (c) Si-piranha/UHMWPE and (b), (d) Si-plasma/UHMWPE films.

The O1s spectra of both piranha- and plasma-treated Si surfaces contain peak components corresponding to O–Si and/or OH groups at 532 eV [19] and O–C group at 533.3 eV [18]. However, the peak area of O–Si is higher and that of O– C is lower, in the case of air–plasma-treated Si when compared to those of the untreated and piranha-treated Si. The low peak area of O–C for plasma-treated Si also supports the effective removal of organic contaminants from Si surface through plasma treatment. The higher peak area at a binding energy (BE) of 532 eV for plasma-treated Si suggests that the air–plasma treatment produces more hydroxyl groups on the Si surface when compared to the untreated and piranha-treated Si [19]. The generation of these hydroxyl groups helps in increasing the surface free energy and thus making the surface more hydrophilic which is expected to improve the adhesion between the polymer film and the surface.

Table 2.
Atomic percents of C and O of piranha- and plasma-treated Si surfaces

Surface	C (%)	O (%)
Si-untreated	17.7	37.6
Si-piranha treated	19.7	34.3
Si-plasma treated	16.9	42.9

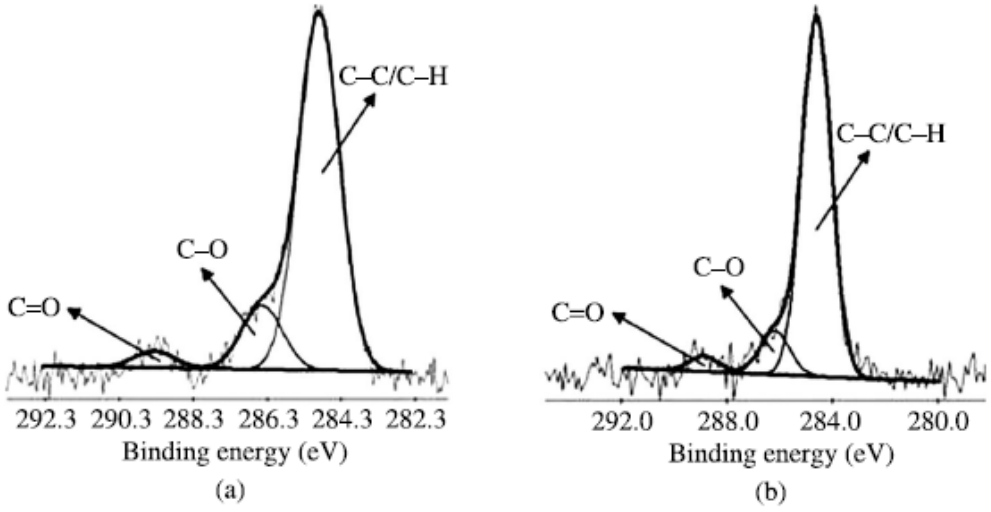

Figure 3. C_{1s} core-level spectra (after curve fitting) of (a) piranha-treated Si and (b) plasma-treated Si.

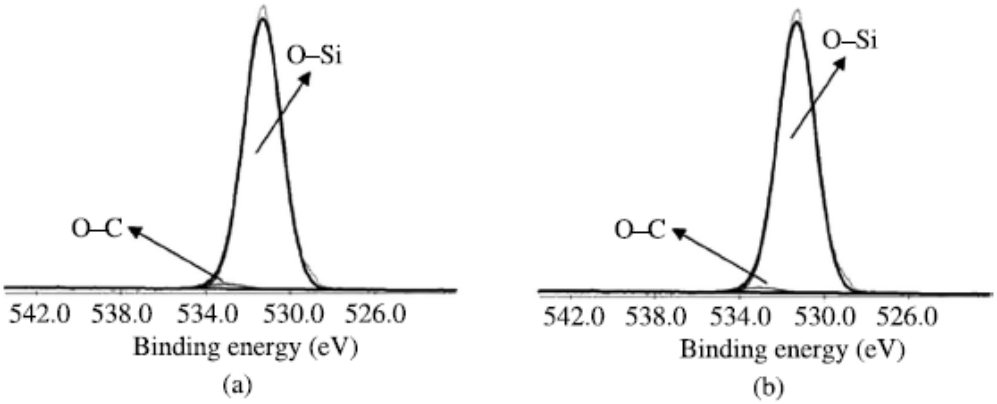

Figure 4. O_{1s} core-level spectra (after curve fitting) of (a) piranha-treated Si and (b) plasma-treated Si.

Table 3.
Curve-fit data and assignments of the peaks for C_{1s} and O_{1s} spectra of untreated, piranha- and plasma-treated Si surfaces

Surface	Core-level spectrum	Binding energy (eV)	Peak assignment	Area (arb. units)	FWHM* (eV)
Si-untreated	C_{1s}	284.6	C–C/C–H	1185	1.30
		286.2	C–O	172	1.30
	O_{1s}	531.9	O–Si	7365	1.60
Si-piranha treated	C_{1s}	284.6	C–C/C–H	1435	1.30
		286.2	C–O	258	1.30
		289.0	C=O	66	1.30
	O_{1s}	532.0	O–Si	6510	1.53
		533.3	O–C	289	1.53
Si-plasma treated	C_{1s}	284.6	C–C/C–H	1031	1.32
		286.2	C–O	131	1.32
		288.9	C=O	47	1.32
	O_{1s}	532.0	O–Si	7414	1.56
		533.3	O–C	133	1.56

* FWHM means full width at half maximum.

3.3. Effect of Pre-treatment on the Adhesion Strength between the UHMWPE Film and the Si Substrate

Scratch tests were performed to investigate the effect of the pre-treatment on the adhesion strength between the UHMWPE film and the Si substrate. Figure 5 shows the FESEM images of scratches made at different loads on Si-untreated/UHMWPE, Si-piranha/UHMWPE and Si-plasma/UHMWPE samples and the corresponding EDS spectra inside the scratches. Results showed that the Si-untreated/UHMWPE and Si-piranha/UHMWPE samples failed at lower critical loads when compared to that of Si-plasma/UHMWPE. UHMWPE film on the untreated and the piranha-treated Si failed at scratch loads of 10 mN and 30 mN, respectively. The EDS spectrum further confirmed the film failure by the presence of Si peak in the peeled off regions. The UHMWPE film on plasma-treated Si failed at a scratch load of ~80 mN, exhibiting a greater scratch resistance. The scratch test results clearly demonstrate that the plasma treatment of Si enhances the adhesion between the UHMWPE film and Si which is much better than that correspondingto piranha-treated Si. The high adhesion strength of UHMWPE film with plasmatreated Si is attributed to the increase in the surface free energy due to the generation of –OH groups on Si as evident from the XPS analysis. As mentioned earlier, the generation of these hydroxyl groups helps in increasing the surface free energy and thus making the surface more hydrophilic which is expected to improve the adhesion between the polymer film and the surface.

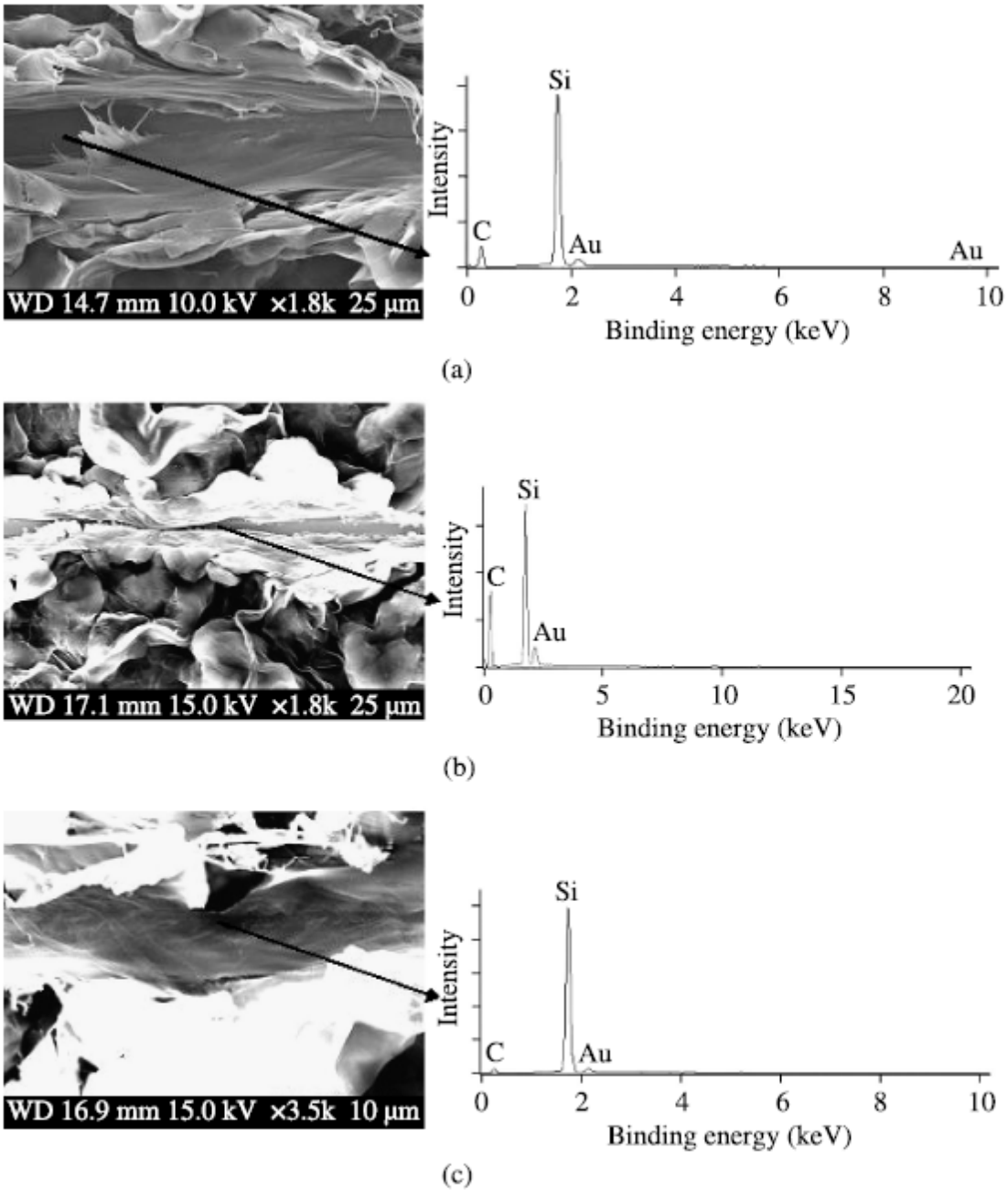

Figure 5. (a) FESEM morphology of a scratch made at 10 mN on Si-untreated/UHMWPE surface and EDS spectrum inside the scratch (right). (b) FESEM morphology of a scratch made at 30 mN on Si-piranha/UHMWPE surface and EDS spectrum inside the scratch (right). (c) FESEM morphology of a scratch made at 80 mN on Si-plasma/UHMWPE surface and EDS spectrum inside the scratch (right).

3.4. Effect of Pre-treatment on the Tribological Properties of the UHMWPE Film

Wear tests were carried out on a ball-on-disk micro-tribometer (CETR Inc., USA) for the Si-piranha/UHMWPE and Si-plasma/UHMWPE samples for comparison purpose. The normal load was kept constant at 1 N and the rotational speed at 200 rpm (0.042 m/s). Ten runs for each condition were conducted. Figure 6 shows the variation of the coefficient of friction with respect to the number of cycles for bare Si, Si-untreated/UHMWPE, Si-piranha/UHMWPE and Si-plasma/UHMWPE samples (typical data). It can be observed that the UHMWPE film on plasma-treated Si demonstrates a higher average wear life (~50 000 cycles) when compared to that of the UHMWPE film coated onto piranha-treated Si (~2000 cycles). This remarkable improvement (~25 times) in wear durability is attributed to the enhanced adhesion between UHMWPE film and plasma-treated Si and UHMWPE film and as demonstrated by the scratch tests. Thus the two tests (scratch and ball-on-disk) have proved that air–plasma treatment of Si is a very costeffective and environmental-friendly method of enhancing the adhesion property of a solid lubricant polymer film to Si substrate.

Figure 7 shows the FESEM/EDS images of the wear track for the bare Si (after 500 cycles), Si-untreated/UHMWPE (after 1000 cycles), Si-piranha/UHMWPE (after 2000 cycles) and Si plasma/UHMWPE (after 10 000 cycles). The respective optical micrographs of the counterface Si3N4 balls are also shown. It can be observed that in the cases of Si-untreated/UHMWPE and Si-piranha/UHMWPE, the film failed after 1000 cycles and 2000 cycles respectively, as is clear from the EDS spectra of the wear tracks in which the Si peak represents the exposed surface of the substrate, indicating the film rupture. It can also be observed that there was a considerable polymer transfer onto the sliding ball, indicating poor adhesion of the film to the substrate. On the contrary, the Si-plasma/UHMWPE film did not fail even after 10 000 cycles as evident from the EDS spectrum. No polymer transfer onto the sliding ball is an indication of the strong adhesion of the polymer film to the substrate.

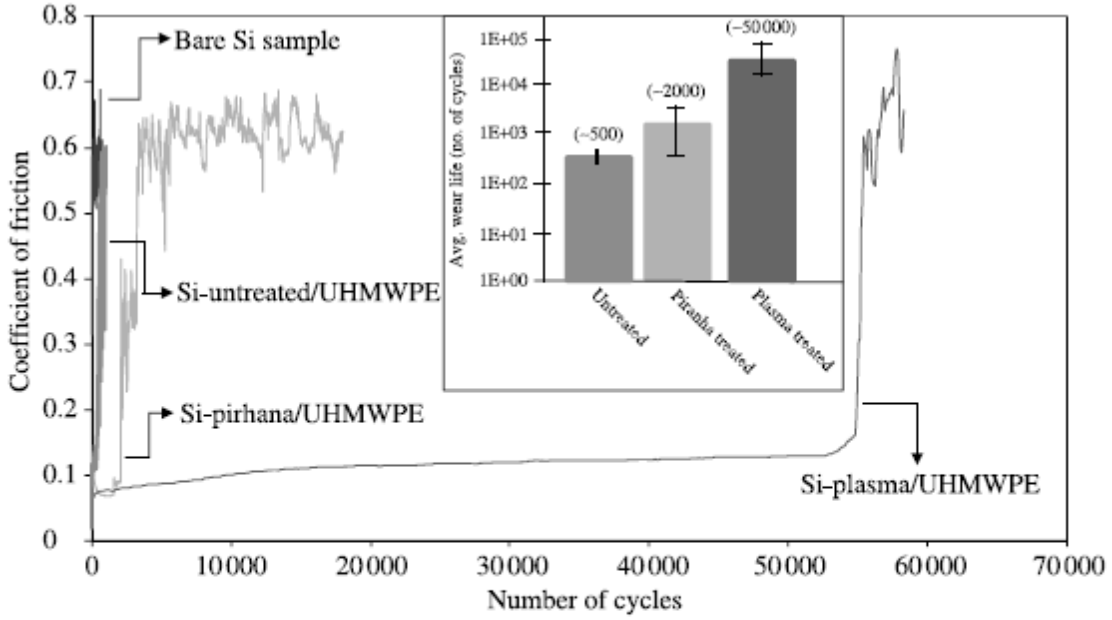

Figure 6. Variation of the coefficient of friction with the number of sliding cycles from typical test runs for bare Si, Si-untreated/UHMWPE, Si-piranha/UHMWPE and Si-plasma/UHMWPE samples. A normal load of 1 N and a rotational speed of 200 rpm (0.042 m/s) were used in the sliding tests. (Inset) Bar graph showing the average wear lives (in terms of number of cycles) for the three different conditions.

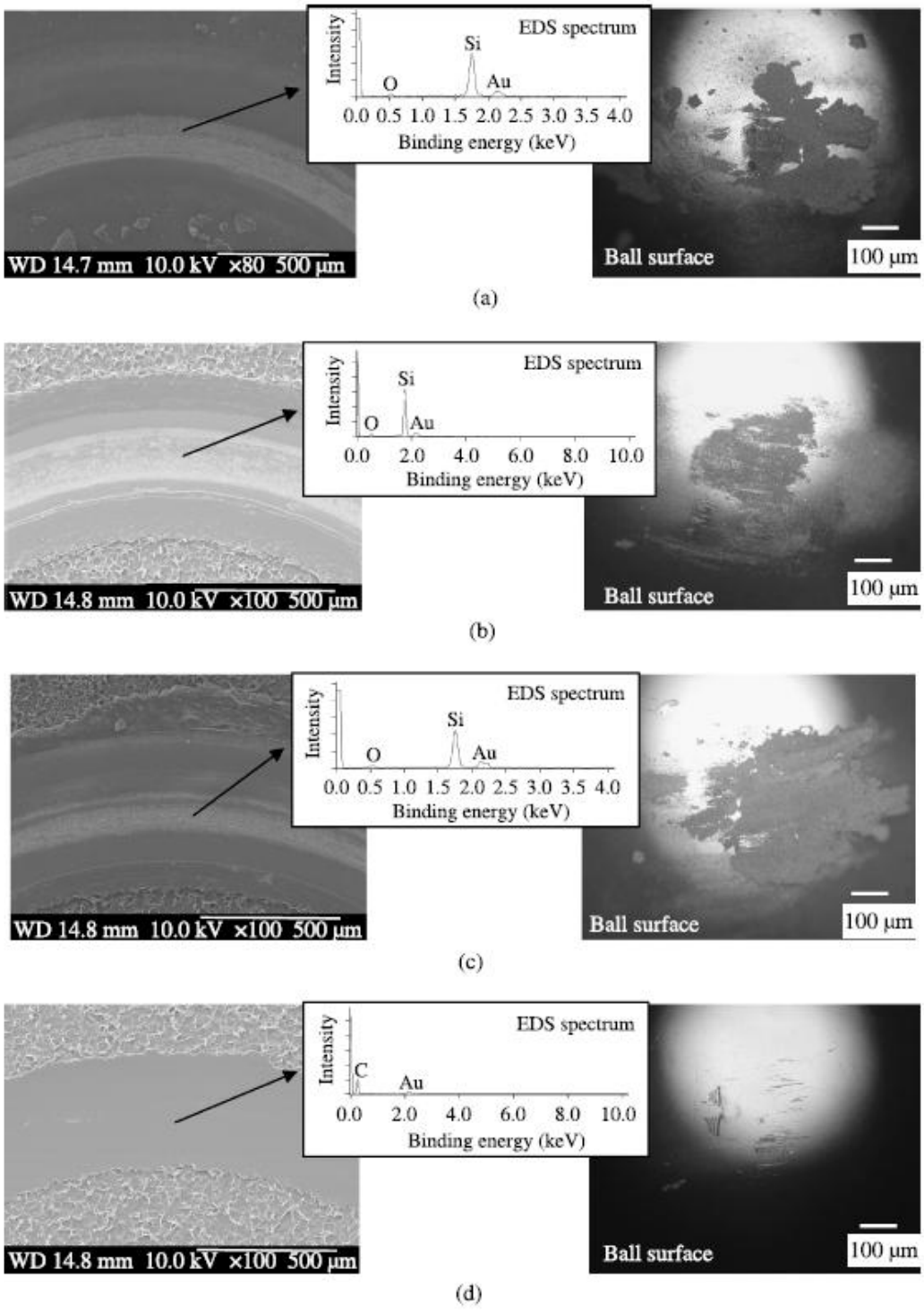

Figure 7. (a) Wear track and ball surface for untreated Si after 500 cycles, (b) wear track and ball surface from Si-untreated/UHMWPE after 1000 cycles, (c) wear track and ball surface from Si-piranha treated/UHMWPE after 2000 cycles and (d) wear track and ball surface from Si-plasma treated/UHMWPE after 10 000 cycles of sliding. For all cases, left picture shows FESEM/EDS image of wear track and the right picture shows optical micrograph of ball surface. A normal load of 1 N and a rotational speed of 200 rpm (linear speed of 0.042 m/s) were used in the sliding tests. All samples were gold coated for conduction improvement for SEM characterization.

4. Conclusions

In the present work, we studied the effect of plasma pre-treatment of Si surface on the wear durability and adhesion properties of UHMWPE film dip-coated onto Si surface and the results were compared with those corresponding to piranha pretreatment of Si surface. Following conclusions are drawn from the present study:

1. Plasma pre-treatment of Si improved the hydrophilic nature of the Si surface (with a water contact angle of 4.3◦) resulting in an increase in the surface free energy when compared to that of the piranha pre-treatment.
2. The plasma pre-treatment of Si enhanced the adhesion between UHMWPE film (15.2–16.6 μm in thickness) and Si surface when compared to that of the piranha treatment of Si. In scratch tests, the critical load of Si-plasma/UHMWPE (∼80 mN) was found to be more than two times of the critical load of Sipiranha/ UHMWPE (∼30 mN).
3. The UHMWPE film coated onto plasma-treated Si showed very high wear durability (∼25 times higher) when compared to the same film coated onto piranha-treated Si which is mainly attributed to the increased adhesion between the UHMWPE film and the plasma-treated Si. In sliding tests against 4 mm diameter silicon nitride ball, Si-plasma/UHMWPE demonstrated an average wear life of ∼50 000 cycles as compared to a wear life of only ∼2000 cycles demonstrated by the Si-plasma/UHMWPE at a normal load of 1 N and a rotational speed of 200 rpm.

Air–plasma pre-treatment of Si can be used for depositing a lubricating layer in MEMS made from Si for higher wear durability as shown in the case of UHMWPE films.

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References

1. V. DePalma and N. Tillman, *Langmuir* **5**, 868–872 (1989).
2. N. Satyanarayana and S. K. Sinha, *J. Phys D: Appl. Phys.* **38**, 3512–3522 (2005).
3. N. Satyanarayana, N. N. Gosvami, S. K. Sinha and M. P. Srinivasan, *Philosophical Magazine* **87**, 3209–3227 (2007).
4. D. B. Asay, M. T. Dugger and S. H. Kim, *Tribology Letters* **29**, 67–74 (2008).
5. J. J. Nainaparampil, K. C. Eapen, J. H. Sanders and A. A. Voevodin, *J. Microelectromechanical*
Systems **16**, 836–843 (2007).
6. J. Zhao, M. Chen, J. Liu and F. Yan, *Thin Solid Films* **517**, 3752–3759 (2009).
7. W. Liu, F. Zhou, L. Yu, M. Chen, B. Li and G. Zhao, *J. Mater. Res.* **17**, 2357–2362 (2002).
8. N. Satyanarayana, S. K. Sinha and B. H. Ong, *Sensors Actuators A* **128**, 98–108 (2006).
9. N. Satyanarayana, S. K. Sinha and L. Shen, *Tribology Letters* **28**, 71–80 (2007).
10. C. Sun, F. Zhou, L. Shi, B. Yu, P. Gao, L. Zhang and W. Liu, *Appl. Surface Sci.* **253**, 1729–1735 (2006).
11. M. Minn and S. K. Sinha, *Surface Coatings Technol.* **202**, 3698–3708 (2008).

12. W. Possart (Ed.), *Adhesion: Current Research and Applications*.Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany (2005).
13. M. Abdul Samad, N. Satyanarayana and S. K. Sinha, *Surface Coatings Technol.* **204**, 1330–1338 (2009).
14. S. P. Khedkar and S. Radhakrishan, *Thin Solid Films* **303**, 167 (1997).
15. H. J. Butt, K. Graf and M. Kappl, *Physics and Chemistry of Interfaces*, 2nd edn, p. 138. Wiley- VCH, Berlin, Germany (2005).
16. R. J. Good, *J. Adhesion Sci. Technol.* **6**, 1269–1302 (1992).
17. K. Miyoshi, *Solid Lubrication Fundamentals and Applications*, p. 266. Marcel Dekker, New York (2001).
18. G. Beamson and D. Briggs, *High Resolution XPS of Organic Polymers: The Scienta ESCA300 Database*, pp. 277–283. John Wiley and Sons, Chicester, UK (1992).
19. M. Kuemmel, J. Allouche, L. Nicole, C. Boissiere, C. Laberty, H. Amenitsch, C. Sanchez and D. Grosso, *Chem. Mater.* **19**, 3717–3725 (2007).