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Frictional behavior on wrinkle patterns of diamond-like carbon films on soft polymer

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ABSTRACT

Frictional behaviors of wrinkle patterns on a diamond-like carbon (DLC) film coated on a soft polymer were investigated. Wrinkle patterns of the DLC layer were formed due to the large difference in elastic moduli between the DLC film and the soft polymer of polydimethylsiloxane (PDMS) as well as high residual compressive stress in the film. The roughness of wrinkled surfaces varied with the thickness of the DLC films, affecting the frictional behaviors. The coefficient of friction significantly reduced as the thickness of the DLC film increased. For lower thicknesses, slip–stick events and surface damages like fish-scales on the wear track were strongly developed. With an increase of sliding distance, a randomly oriented wrinkle pattern was getting worn on its top surfaces, resulting in an increase of the contact area as well as a coefficient of friction (COF). However, for thicker films simple wear was observed with the lower COF due to DLC nature.

1. Introduction

Friction behaviors on soft materials rubbing against hard objects have been studied to avoid undesirable surface damages such as wear and plowing, which are known to increase the frictional coefficient and to cause the unsteady frictional behavior known as the 'stick-slip' phenomena [1,2]. To prolong the lifetimes of related applications of soft substances such as windscreen wipers, tires, human skin, or polymeric devices for MEMS sensors and actuators, surface treatments or hard coatings have been suggested as protective layers against friction, wear, or impact [3,4]. Among several hard coatings, diamond-like carbons (DLC) films have been heavily studied as protective layers coated on various materials, such as metals and ceramics, as well as polymers in various applications, due to their chemical inertness, biocompatibility and hemo-compatibility [3,5,6]. Recently DLC coatings have been applied as hard and anti-frictional coatings on soft polymeric materials like rubbers. These coatings would improve surface chemical properties and mechanical performance by reducing friction and wear [7–10]. Mostly, for lowering a lower coefficient of friction (COF), DLC coated soft polymers have been studied with an emphasis on the deposition conditions such as the film density, interface adhesion, hydrocarbon precursors or doping materials. However, the roughness effect on mechanical performance of DLC films coated on soft polymers was not well explored.

Recently researchers have investigated the frictional behaviors of DLC films on hard materials with an emphasis on the surface roughness. It was reported that the nano-undulated surface could suppress the tribo-chemical reaction between the film surface and the counterface ball, resulting in a reduced COF in ambient air [10,11,12]. Furthermore, the surface roughness was reported to reduce the COF by suppressing wear particle generation, removing the wear particles from the sliding interface and preventing the agglomeration of wear particles [13,14]. The reduced contact area between the sliding ball and the rough target surface also decreased the COF and wear rate [15].

In the present work, we explore the frictional behaviors on the wrinkled surfaces of thin compressive DLC films coated on a soft polymer of PDMS using radio-frequency plasma enhanced chemical vapor deposition (r.-f. PECVD). A thin DLC film retains the residual compressive stress in the coating layer, which can directly produce nanoscale wrinkle patterns on soft polymeric surfaces. In general, wrinkle patterns as a surface texture can be generated in a thin hard film supported on a compliant (or soft) substrate when the film is compressed laterally and buckled [16].

Surface roughness of the wrinkled thin DLC film varied with respect to the deposition time of the DLC films. When a DLC film is coated on a relatively soft polymer of polydimethylsiloxane (PDMS), wrinkle patterns with a certain roughness as shown in Fig. 1 can be evolved due to a large difference in the elastic moduli (100 GPa for DLC, 1 MPa for PDMS) as well as high compressive stress (~1 GPa) in the DLC films. Friction behaviors were explored by using a tribo-test to measure the COF. The wear track was carefully characterized for different thicknesses of DLC films on PDMS with varying sliding speeds.

2. Experimental details

DLC films were deposited on PDMS substrates to form wrinkle patterns, as well on thin Si strips for the measurement of stress, by the following procedures. PDMS was prepared by mixing an

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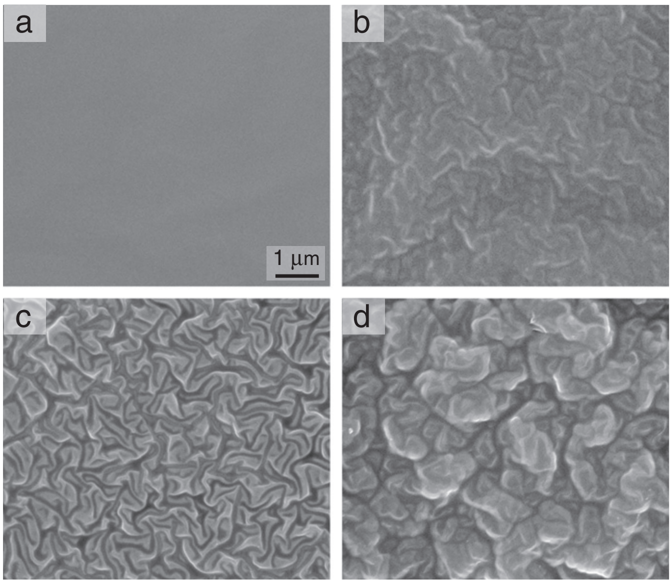

Fig. 1. SEM images of PDMS (a) and wrinkled surfaces after the deposition of DLC films with thicknesses of (b) 3 nm, (c) 24 nm and (d) 213 nm.

elastomer and a cross-linker in a mass ratio of 10:1 (Sylgrad, 184 Kit, Dow corning), then poured into a plastic container with a flat surface and degassed in a vacuum chamber, followed by curing at 70 °C on a hot plate for 2 h. Samples of PDMS were cut for the experiment with a uniform size of 50.0 mm × 50.0 mm × 5.0 mm, then placed on the cathode of the PECVD chamber for DLC coating.

The DLC films were deposited on PDMS and Si strips by a 13.56 MHz r.-f. PECVD technique. Prior to the deposition of DLC films, a pretreatment using oxygen plasma was performed on all substrates at a bias voltage of −400 V and a pressure of 1.3 Pa for 1 min to promote better adhesion between DLC and PDMS substrates. The treatment time was sufficient to develop higher adhesion between the DLC film and PDMS and to avoid nanostructure formation on PDMS by plasma irradiation. Then, DLC was deposited with a precursor gas of methane using the same bias voltage of −400 V and pressure of 1.3 Pa. Deposition times were chosen to range from 10 s to 120 min, resulting in film thicknesses from about 1 nm to 372 nm as measured by an atomic force microscrope (AFM, Parksystem).

In order to evaluate the residual stress, DLC films were also deposited on a series of Si strips of 100 μm in thickness with the same deposition conditions as those on PDMS. The root mean square (RMS) roughness values of DLC films deposited on flat Si and PDMS substrates were estimated. Frictional behaviors were investigated by using a homemade ball-on-disk type wear rig installed inside an environmental chamber [17]. The steel bearing ball (AISI 52100) of 6 mm in diameter was set up to slide over the DLC wrinkle surface with various sliding speeds from 4.8 to 477.5 RPM, or linear speeds from 5 to 500 mm/s, with the rotating radius of 10 mm, and the normal load of 1 N. The maximum sliding distance of the tribology test was fixed at 550 m. The tribo-tests were performed at room temperature with fixed relative humidity (RH) of 20–30%. The surface morphologies of wrinkled DLC surfaces before and after the wear test were observed using AFM and scanning electron microscopy (SEM, NanoSEM, FEI company).

3. Results and discussion

Upon depositing the DLC film on PDMS, a wrinkle pattern forms in order to release the strain energy of the DLC film accumulated by residual compression, as shown in Fig. 1 [18]. Randomly oriented wrinkle structure is clearly seen after deposition of the DLC thin film on PDMS due to the equi-biaxial nature of compressive stress in the film [19]. As the deposition time is increased, the nanoscale roughness is covered by continuous deposition of amorphous carbon, while microscale roughness appears on the surface after about 11 nm of deposition (Fig. 2a).

In addition to providing a high compressive mismatch strain in the film, deposition of a DLC film on a PDMS substrate also provides a big difference in elastic moduli between the film and substrate, resulting in wrinkle patterns in the DLC film. The wrinkle wavelength (λ) of a stiff thin film of thickness (t), formed under the plane-strain condition, is determined as

$$\lambda = 2\pi t\left[\frac{\left(1-v_s^2\right)E_f}{3\left(1-v_f^2\right)E_s}\right]^{1/3} \tag{1}$$

where E_s and E_f are Young's moduli and v_s and v_f are Poisson's ratios with the subscripts s and f denoting the substrate and film, respectively [20]. In addition, the critical compressive strain (e_c) to induce wrinkling is calculated as

$$e_c \approx 0.52\left[\frac{\left(1-v_f^2\right)E_s}{\left(1-v_s^2\right)E_f}\right]^{2/3} \tag{2}$$

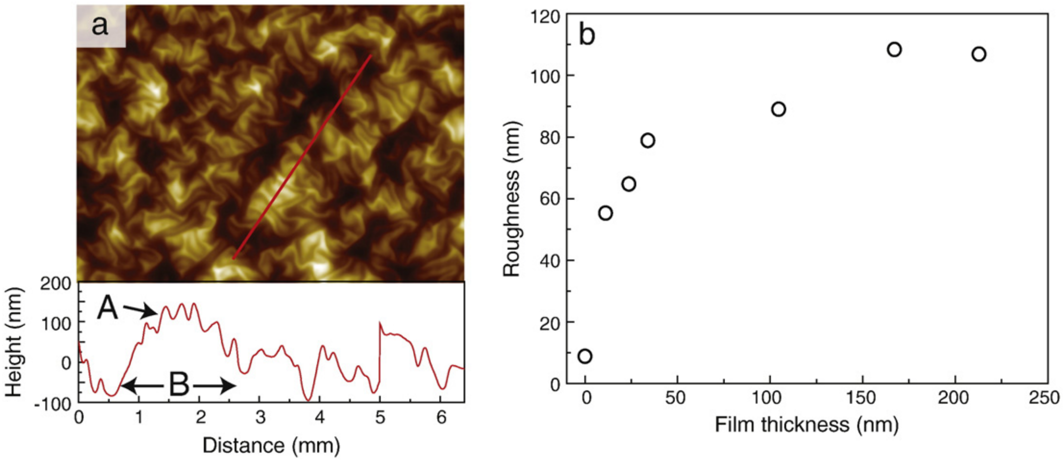

Fig. 2. (a) An AFM image of the DLC with a thickness of 24 nm. A cross-sectional profile along the red line on the AFM image shows a hierarchical wrinkle structure consisting of primary wrinkle (A) with a wavelength of 325 nm and secondary (B) with 2.1 μm wavelength. (b) Measured roughness on wrinkled surfaces with respect to the thickness of DLC film. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

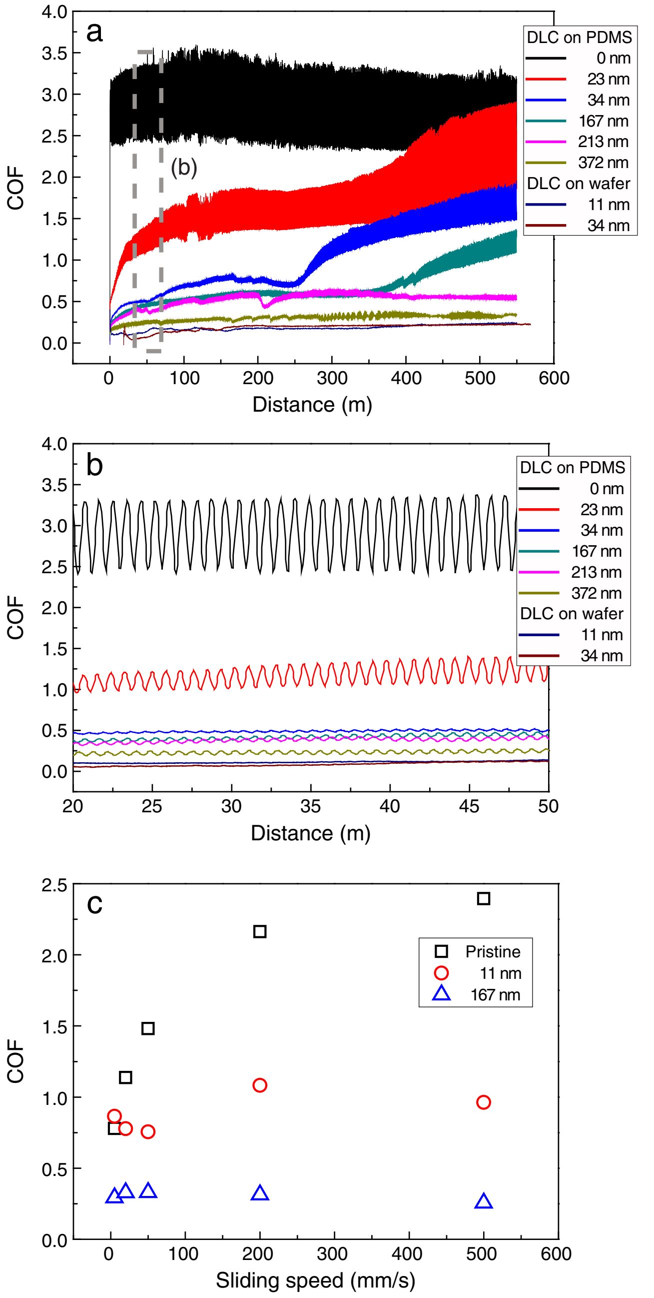

Fig. 3. (a) Variation of COF with respect to the thickness of DLC films coated on PDMS and flat Si-wafer. (b) Magnified view of (a) showing the decrease of stick–slip phenomena due to increasing deposition thickness. (c) The COF with different linear sliding speeds of steel ball, clearly showing the viscoelastic property of PDMS, was significantly reduced with increasing deposition thickness.

for strong elastic moduli mismatch, i.e. $E_s/E_f << 1$, where e_c is the critical compressive strain to form a wrinkled structure with the specific wavelength expressed in Eq. (1).

The mechanical properties of the DLC film deposited from CH_4 by using the PECVD method were measured for a compressive stress of ~1 GPa. A Young's modulus of ~100 GPa with a Poisson's ratio of 0.32 was taken from the previous work [16,21], resulting in a compressive strain of e_c ~0.042%. The DLC film generates a mismatch compressive stress (σ) during the deposition process, equivalent to lateral compressive strain $e = \sigma/(E/(1-\upsilon^2))$ ~0.90% on the film, which greatly exceeds the critical compressive strain e_c ~0.042% to cause highly nonlinear wrinkle patterns on PDMS. As DLC film is deposited on a compliant PDMS substrate with a Young's modulus of approximately 2 MPa and Poisson's ratio of 0.48 [4], the highly mismatched elastic properties determine the primary wavelength of the wrinkle from Eq. (1) as ~152t, which matches in dimension with the measured wavelength of ~300 nm for the film thickness of ~3 nm as shown in Fig. 1b. Because of the high relative strain of the DLC film, a highly nonlinear wrinkle pattern was observed with a dual wavelength of a nanoscale primary (A) wavelength of 325 nm nested on a microscale secondary (B) wavelength of 2.1 μm as shown in Fig. 2a. It was shown that the roughness of coated PDMS increases rapidly as film thickness increases. However, the increase of roughness almost saturates on films with thicknesses of 40 nm and above, showing that the roughness formed during the early deposition process becomes smoothed by the continuous deposition of coating, as shown in Fig. 2b [22].

3.1. Frictional behaviors with deposition time

The frictional behavior in ambient air was characterized by measuring the coefficient of friction (COF) and the surface morphologies on the wear track of the DLC films on PDMS substrates was shown in Figs. 3–6. In ambient air with a relative humidity of 20–30%, the COF increased gradually during the run-in stage and reached and maintained a steady value during the steady-state stage as shown in Fig. 3a. As an instance, the steady-state stage for the case of 23 nm occurs for distances of 150 m up to 300 m. The average COF in the steady state reduced from 1.5 to 0.5 as the deposition thickness was increased up to 213 nm. Note that the COF on the pristine PDMS was measured to be 2.4 at the sliding speed of 286 mm/s.

The stick–slip phenomenon was clearly observed on bare PDMS, as shown in Fig. 3b. The stick–slip phenomenon for a soft substrate rubbed by a hard material of high asperity has been extensively studied, focusing on the transition from steady slip to the stick–slip phenomenon [23,24]. This transition was explained as the onset of the non-steady motion of a sliding ball, which was caused by the effects of wear and plowing of relatively soft substrates during a tribology experiment. The stick–slip phenomenon, which was usually known to cause undesired effects such as increased wear rate and noise on the substrate, was significantly reduced with the increase of film thickness as shown in Fig. 3a. Fig. 3b, the magnified graph of Fig. 3a, shows oscillations in the COF which reveal the amplitude of stick–slip in the steady state. As the DLC film was fully worn by the sliding ball, stick–slip quickly recovered with the increase of COF in Fig. 3a. As the film thickness increased, the onset of stick–slip was delayed.

In Fig. 3c, the COF of DLC film with a thickness of 167 nm was shown not to depend on the sliding speed of the tribo-ball, for sliding speeds in the range from 5 to 500 mm/s. In contrast, the COF of bare PDMS was drastically changed from 0.75 to 2.5 as the speed varied from 5 to 500 mm/s for the sliding distance of 10 m as shown in Fig. 3c. The dependence of frictional characteristics on sliding speed has been widely studied [25,26] and is known to be effected by the viscoelastic property of the material, which describes how the frictional force is affected by the strain rate ($\dot{e}$). This effect is usually expressed as the viscous shear stress relation, shear stress ~$\mu\dot{e}$, where μ is viscosity. The viscosity of bare PDMS, which is tuned by temperature change, was also reported to change the COF [27].

Low COF can be explained by observation of the wear track on the DLC (103 nm in thickness) coated PDMS. Fig. 4 indicates flattening sequence taken from SEM images of normal (Fig. 4a–c) and oblique view (Fig. 4d–f, 40° tilted from surface normal) for different sliding distances of 0, 100 and 550 m, respectively. The wear track showed significant change from wrinkled surface to flattened surface before and after sliding, respectively, due to the surface wear by the sliding ball. A randomly oriented wrinkle pattern was worn on its top surfaces at a sliding distance of 550 m, indicating that the contacting

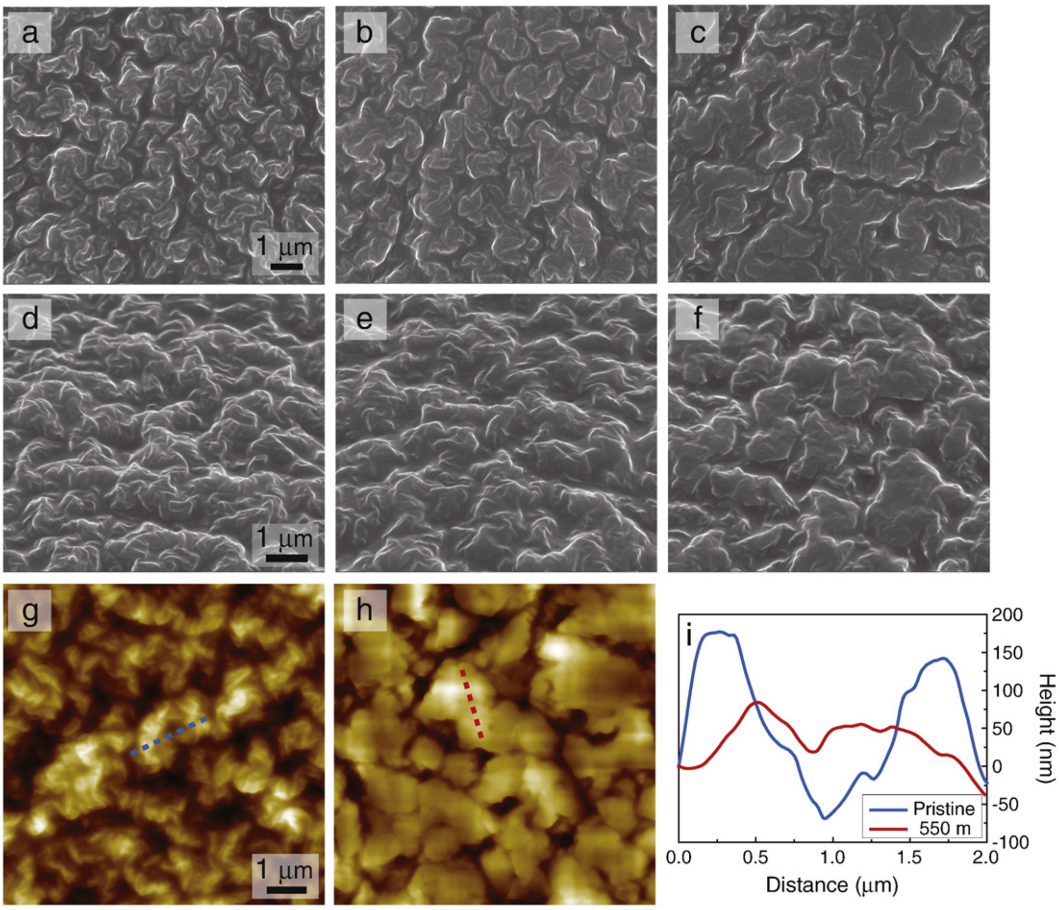

Fig. 4. SEM images of (a–c) normal and (d–f) oblique view for flattening sequence on wrinkled surface with the deposition thickness of 103 nm for sliding distances of 0, 100, and 550 m. Representative surface profiles on top part were taken dotted line of AFM images of (g) pristine wrinkled surface and (h) flattened surface at 550 m wear track. (i) Comparison of surface profiles on top parts, indicating geometrical change and a decrease in surface roughness.

area would be larger for the flattened surface than that for the wrinkled surface. This flattened top surface of the wrinkled DLC film was further analyzed using AFM to compare representative surface profiles on top surface between pristine wrinkled surface (Fig. 4g) and flattened surface taken at sliding distance of 550 m (Fig. 4h). Representative surface profiles between before and after (at 550 mm) tribology test clearly shows a decrease of the roughness from 85 to 23 nm, indicating an increase of the contact area while the overall roughness slightly decreases from 107.3 to 92 nm. It can be considered that the increase in the contact area between the sliding ball and the counter surface results in the increase in COF from 0.75 to 1.04.

Fig. 5 clearly shows the decreasing tendency of the COF in relation to increasing values of deposition thickness (Fig. 5a) and surface roughness (Fig. 5b) due to the effect of reduced contact area. Plowing was significantly observed on the wear track of the bare PDMS and PDMS with thin DLC coatings of less than 167 nm after a sliding distance of 550 m as shown in Fig. 6. Fish-scale surface damage on thinner DLC coatings should be understood by considering the sliding process of a steel ball on PDMS. As a steel ball slides over PDMS with constant load at constant speed, the normal force on the viscoelastic PDMS material due to the load causes it to pile up ahead of the ball. As the ball moves further, the PDMS material is accumulated further, increasing resistance to the ball moving forward so that it drags along the surfaces, which causes an increase of the COF [28,29]. The well-known 'stick–slip' phenomenon can be observed as the ball undergoes repeated changes in dragging force, leading to the ball repeatedly sticking and releasing at a constant sliding speed. As the sliding distance increases further, the sliding ball will release the PDMS material as the DLC is worn out and then slip. By dragging of the applied normal load, the ball would repeatedly stick and slip over the material, which causes permanent damage, such as fish-scale damage, on the DLC coated PDMS. On the thicker film, no apparent event (except for wearing) was observed since the substrate effect was not dominant at this condition, resulting in a lower COF, which was comparable to that of DLC coated on a flat Si wafer.

4. Conclusions

Wrinkle patterns were observed in DLC films coated on a very compliant substrate of PDMS with various thicknesses from 1 to several hundred nm. As the film has a high compressive stress that is retained during the film deposition process, as well as a bigger elastic modulus than that of soft PDMS, a wrinkle pattern is formed on the PDMS during the deposition process in the PECVD system. The roughness of wrinkle patterns varied with increasing deposition time. The COF decreased with increasing deposition time of the DLC film, in comparison to the uncoated pristine PDMS. In particular, strong stick–slip behavior and high COF values were explored through the effect of the compliance of the PDMS substrate, which was shown in bare PDMS and thin DLC coated surfaces. Significant reduction of the COF was measured with increasing deposition thickness of DLC. It was found that the wrinkled top surface of the DLC coated PDMS was getting worn by a steel ball during tribology test, resulting in the reduction of the surface roughness or the

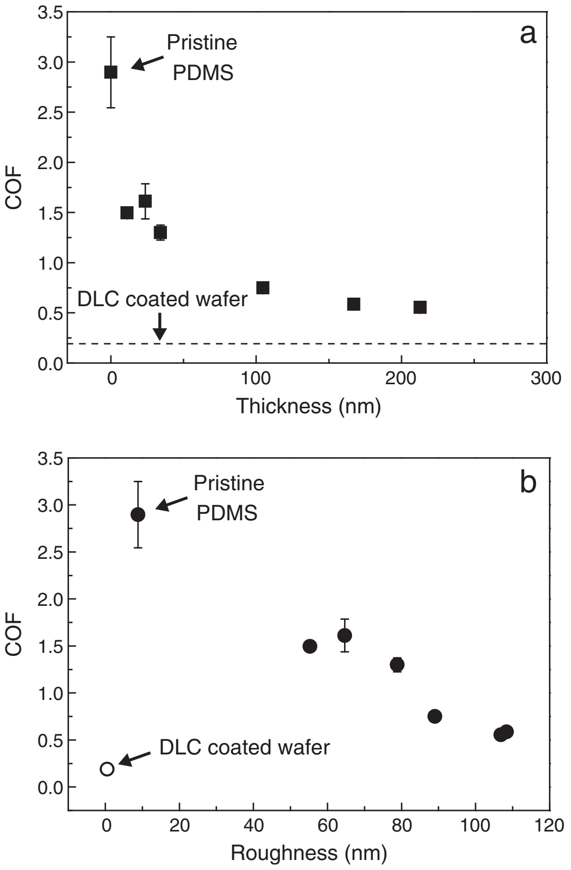

Fig. 5. Graphs showing the COF varying with (a) the DLC film thickness and (b) the surface roughness. The DLC thickness on the wafer was fixed as 34 nm.

increase of the contact area, which would explain the increase of the COF.

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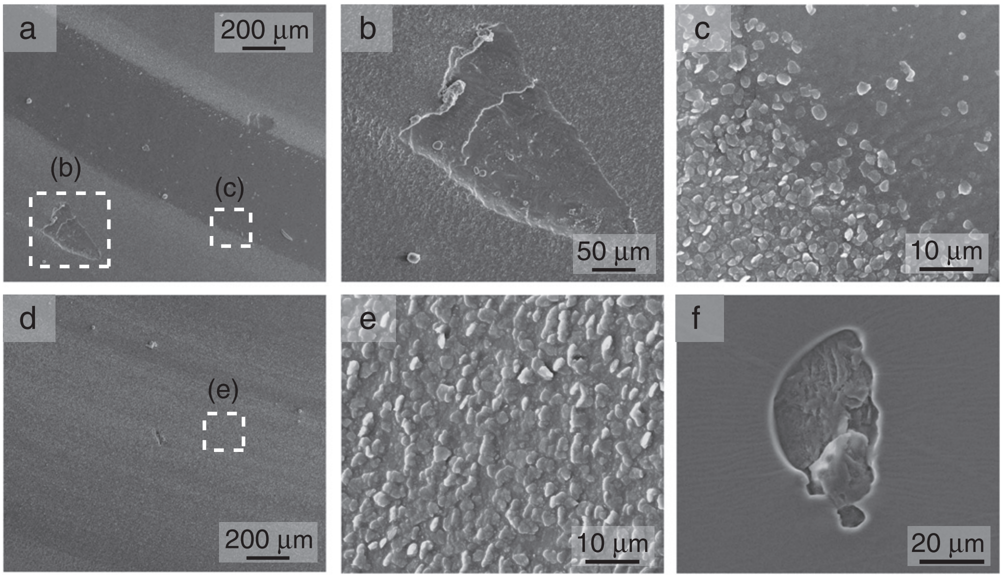

Fig. 6. SEM images of wear tracks after the tribology test with a DLC film thickness of (a) 105 nm, on which (b) partial and (c) full surface damages were shown at a sliding distance of 550 m. The wear track for DLC film with a thickness of (d) 213 nm, on which (e) no significant surface damage was observed at same sliding distance. (f) Surface damage found on bare PDMS at sliding distance of 550 m.