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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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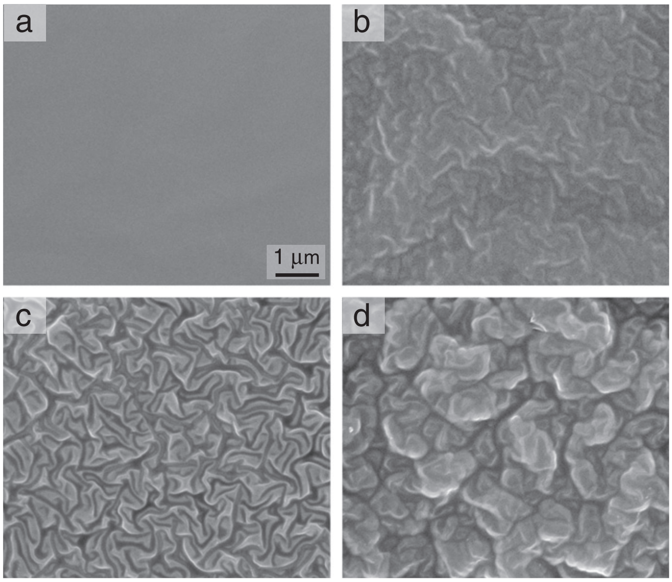

Fig. 1. SEM images of PDMS (a) and wrinkled surfaces after the deposition of DLC films with thicknesses of (b) 3 nm, (c) 24 nm and (d) 213 nm.

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

$$\lambda = 2\pi t\left[\frac{\left(1-\nu_s^2\right)E_f}{3\left(1-\nu_f^2\right)E_s}\right]^{1/3} \qquad (1)$$

where E_s and E_f are Young's moduli and ν_s and ν_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

$$e_c \approx 0.52\left[\frac{\left(1-\nu_f^2\right)E_s}{\left(1-\nu_s^2\right)E_f}\right]^{2/3} \qquad (2)$$

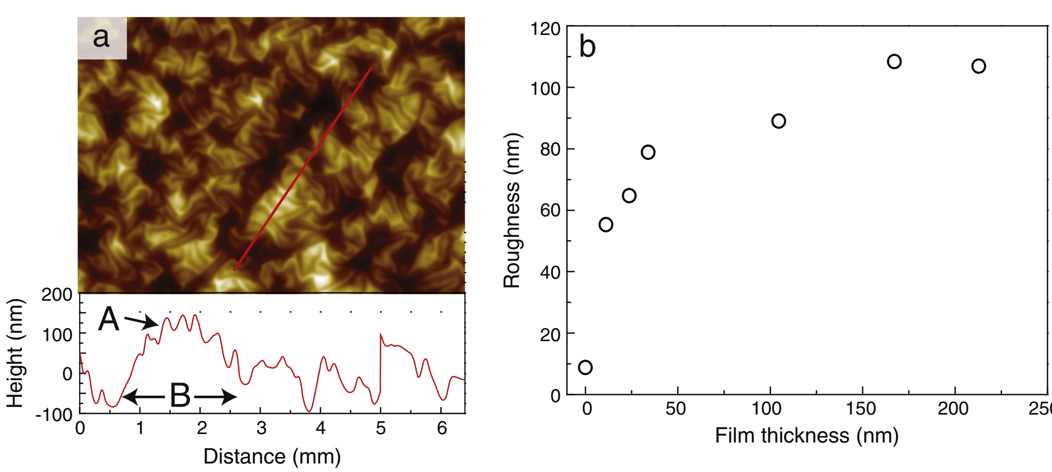

Fig. 2. (a) An AFM image of the DLC with a thickness of 24 nm. A cross-sectional profile along the red line on the AFM image shows a hierarchical wrinkle structure consisting of primary wrinkle (A) with a wavelength of 325 nm and secondary (B) with 2.1 µm wavelength. (b) Measured roughness on wrinkled surfaces with respect to the thickness of DLC film.