

Self-Assembly and Tribological Property of a Novel 3-Layer Organic Film on Silicon Wafer with Polydopamine Coating as the Interlayer

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A novel 3-layer organic film was fabricated on silicon wafer with a polydopamine coating (coded as PDAC) as the interlayer by a multistep self-assembly process. The formation and structure of the films were analyzed by means of ellipsometric thickness measurement, water contact angle measurement, and attenuated total reflection-Fourier transform infrared spectrometry (ATR-FTIR). Meanwhile, an atomic force microscope (AFM) characterization was performed to evaluate the adhesive and microtribological behaviors of the 3-layer film, and a ball-on-plate tribometer was used to test macrotribological performance. As results show, the as-prepared 3-layer film possessed the excellent tribological properties characterized by lower friction and higher antiwear ability, which was ascribed to the special chemical structure of the film, i.e., the strong adhesion of the film to the silicon wafer, the chemical bonding between the adjacent layers, the cross-linked structure of the PDAC interlayer, and the hydrophobicity, high flexibility, and high elasticity of the stearyl chloride (STC) outer layer. Hopefully, the present work provides a feasible route to construct a multilayer film with excellent structural stability and tribological behavior. The titled multilayer film might find potential applications in boundary lubrication and many other areas.

I. Introduction

Due to good thermal resistance and flexibility,^{1–3} polymeric thin film has been used as a boundary lubricant coating in many fields including microelectromechanical systems (MEMS),⁴ artificial joints,⁵ computer hard disks,⁶ etc. However, two main factors should be considered in employing polymeric film as a good boundary lubrication coating. One is the bonding strength of the polymer molecules with the substrate, and the other is the surface physicochemical properties of the polymeric film. For example, polymer thin films adhered to the substrates through weak bonding are easily peeled off during friction,⁷ while those with high surface energy generally exhibit poor lubrication ability.^{8–19}

Recently, dopamine has been demonstrated to be an effective adhesive that can be attached to almost all material surfaces and autopolymerized to form polydopamine coating (coded as PDAC). The process of preparing PDAC is simple, and the physicochemical properties of PDAC can be well controlled by further chemical modification,²⁰ making it feasible for PDAC to be employed in boundary lubrication. However, PDAC on an inorganic substrate is less stable than that on an organic surface.²⁰ It is imperative to premodify the inorganic substrate using an organic layer to improve the bonding strength between the PDAC and the substrate.^{21–23} For that purpose, a self-assembled monolayer (abridged as SAM) of 3-aminopropyl triethoxysilane (coded as APTS) was self-assembled on a silicon surface to enhance the adhesion of PDAC thereon, which was based on the following consideration: the self-assembly of APTS

monolayer on the Si substrate is fulfilled through forming stable Si–O–Si covalent bonds, which makes it feasible for dopamine molecules to be fixed on the Si substrate coated with APTS-SAM, forming firm PDAC by special chemical reaction.²⁰ However, it should be noted that the employment of PDAC as a boundary lubricant coating is highly restricted due to the presence of a large number of polar amino groups ($-\text{NH}_2$) on the surface. Films with polar groups (such as $-\text{COOH}$,^{8–11} $-\text{OH}$,^{12,13} and $-\text{NH}_2$ ^{14–19}) exposed to the outside generally possess worse tribological properties characterized by higher friction and decreased antiwear ability than those with apolar groups (such as $-\text{CF}_3$ ¹⁴ and $-\text{CH}_3$ ^{8,14–18}). A feasible method to improve the tribological properties of thin films with outer polar groups is chemo-grafting a new layer with outer apolar groups on top of the surface. Employing this notion, a series of self-assembled dual-layer films have been prepared in our group, and it was found that they possessed improved antiwear ability and lower friction.^{14–19} As a part of continuing efforts pursuing novel thin organic films with improved tribological behaviors, especially the antiwear life, a self-assembled 3-layer organic film with a PDAC as the interlayer and a stearyl chloride (STC) single layer as the outer layer was prepared on the silicon surface. Then, the microstructure and tribological behavior of the 3-layer film were investigated in relation to its chemical composition and structure, aiming at developing thin-film lubricants suitable for MEMS and other devices.

2. Experimental Section

2.1. Materials. 3-Hydroxytyramine hydrochloride (dopamine hydrochloride, 99%), 3-aminopropyl triethoxysilane (99%), and tris(hydroxymethyl) aminomethane (99.8%, coded as TRIS) were purchased from Acros Organics. Stearyl chloride (STC, $n\text{-C}_{17}\text{H}_{35}\text{COCl}$) was purchased from Tokyo Kasei Kogyo Co., Ltd. (Tokyo, Japan). All other reagents are analytical grade and

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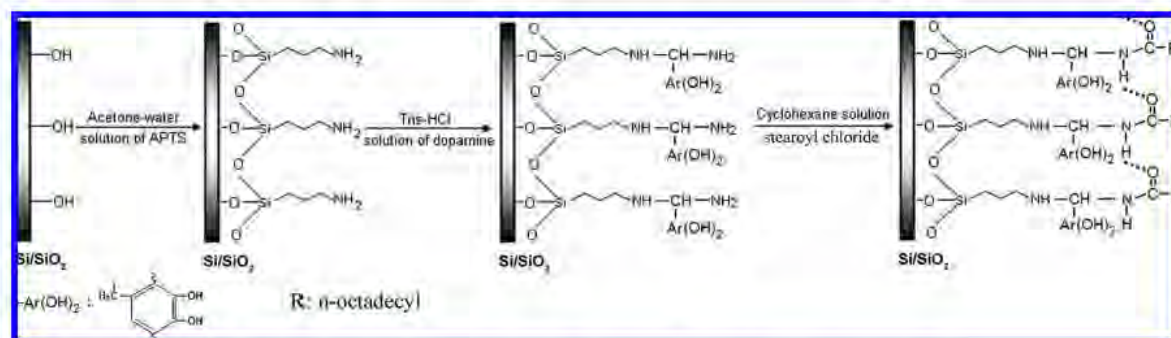


Figure 1. A schematic view of the formation and combination bonding of the 3-layer film on silicon wafer.

were used as received. P-type polished single-crystal silicon (111) wafers were obtained from the GRINM Semiconductor Materials Company (Beijing, China). Ultrapure water ($>18\text{ M}\Omega$) was used in this work.

2.2. Preparation of the 3-Layer Film. Silicon wafers were cleaned and hydroxylated in piranha solution (a mixture of 7:3 (v/v) 98% H_2SO_4 and 30% H_2O_2) at $90\text{ }^\circ\text{C}$ for 30 min. After being rinsed with ultrapure water and blown dry with N_2 , the silicon wafers were placed in freshly prepared APTS solution (5 mM, obtained by dissolving a certain amount of APTS in a mixture of acetone and water with a volume ratio of 5:1). After being immersed in the APTS solution for 30 min, the wafers were taken out of the solution and sonicated in ultrapure water for 2 min, generating the desired APTS-SAM thereon.

The PDAC was prepared according to the method reported in the literature.²⁰ Briefly, 0.05 g of dopamine was first dissolved in 25 mL of TRIS-HCl aqueous solution (10 mM, pH 8.5) and then the APTS-SAM modified silicon wafers were dipped into this solution for 6 h, allowing the formation of desired PDAC atop APTS-SAM. The silicon wafers were then ultrasonically cleaned in ultrapure water for 5 min and blown dry with N_2 , and the obtained dual-layer film was defined as APTS-PDAC.

Silicon substrate modified by APTS-PDAC was immersed into a cyclohexane solution of STC (10 mM, containing $5\text{ }\mu\text{L}$ of triethylamine) for 24 h, then ultrasonically cleaned in toluene and acetone, in succession, and rinsed with ultrapure water and blown dry with N_2 . The resulting 3-layer film was defined as APTS-PDAC-C18. For comparison, the APTS-C18 dual-layer film was prepared by a similar procedure that omitted the deposition of PDAC.

2.3. Characterization. The static water contact angle of the film samples was determined with a DSA100 contact angle meter (Kruss, Germany) and the averaged values of at least three repeat measurements for each sample are reported. The thickness of the film was measured with a Gaertner L116-E ellipsometer equipped with a He-Ne laser (632.8 nm) set at an incident angle of 50° . Attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectra of the thin films were recorded with an IFS 66 V/S Fourier transformation infrared spectrometer (Bruker, Germany), using a Harrick Scientific horizontal reflection Ge-attenuated total reflection accessory (GATR, incidence angle 65°). The samples were placed in contact with the flat surface of a semispherical Ge crystal as the optical element. The spectra were collected for 32 scans with a resolution of 4 cm^{-1} and the background was collected by using the accessory in the absence of the samples. To eliminate the effect of H_2O and CO_2 , the pressure in the sample chamber and optical chamber was kept below $6.0 \times 10^{-4}\text{ MPa}$. The surface morphology and microstructure of the thin films were observed in tapping mode with a Nanoscope IIIa multimode atomic force microscope (AFM, Veeco, USA).

TABLE 1: Water Contact Angle and Thickness for the Silica Layer and the Modified Silicon Surfaces

test samples	water contact angle (deg)	thickness (nm)
Si/SiO_2	~ 0	3.2
APTS-SAM	49.6	0.7
APTS-PDAC	54.1	13.5 ^a
APTS-PDAC-C18	96.5	2.1 ^b

^a 13.5 nm was the thickness of the PDAC layer. ^b 2.1 nm was the thickness of STC layer.

2.4. Tribological Property. The microtribological properties of the prepared thin films were measured with the same AFM in contact mode. Triangle-shaped silicon nitride cantilevers with a normal force constant of 2 N/m were employed for AFM measurements. No attempt was made to calibrate the torsional force constant and the same cantilever was applied for all measurements. The output voltages were directly used as relative frictional force. A series of measurements of the friction-load relationship were made from friction loops obtained from at least five separate locations on each sample surface. To obtain the adhesive force between the AFM tip and the film surface, the force-distance curve was recorded on a CSPM 4000 atomic force microscope (AFM, Being Nano-Instrument, China) and the pull-off force was reckoned as the adhesive force. All experiments were carried out under ambient conditions of $28\text{ }^\circ\text{C}$ and 25% RH.

Macrotribological tests were run on a UMT-2MT tribometer (USA, CETR) in a ball-on-plate contact configuration. Commercially available steel balls ($\phi = 3\text{ mm}$) were used as the stationary upper counterparts, while the lower silicon wafers coated with the thin films were mounted onto the flat base and driven to reciprocally slide at a distance of 0.5 cm. The friction coefficient-versus-time curves were recorded automatically. At least three repeat measurements were performed for each frictional pair. The friction coefficient and antiwear life were measured at a relative error of $\pm 10\%$ and $\pm 5\%$, respectively.

3. Results and Discussion

3.1. Formation and Characterization of the 3-Layer Film.

As schematically illustrated in Figure 1, a novel 3-layer film of APTS-PDAC-C18 was constructed on the silicon surface through a multistep self-assembly process. First, APTS-SAM was introduced onto the silicon surface. Then, dopamine was chemically adsorbed onto the amino-terminated surface and polymerized to form PDAC.²⁰ At last, the PDAC surface was further modified by chemo-grafting a monolayer of STC to attain the 3-layer film of APTS-PDAC-C18.

Formation of APTS-SAM was characterized by thickness and water contact angle measurements. As shown in Table 1, the thickness of the APTS-SAM is 0.7 nm. Assuming that the length

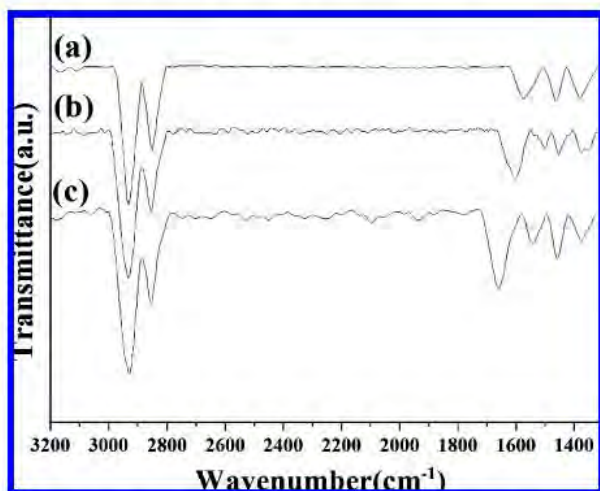


Figure 2. ATR-FTIR spectra of various films: (a) APTS-SAM, (b) APTS-PDAc, and (c) APTS-PDAc-C18.

of one $-\text{NH}_2$ unit is equal to that of one $-\text{CH}_2$ group (about 0.14 nm in all-trans configuration chains),²⁴ an integrated monolayer of APTS-SAM has a theoretical thickness of about 0.6 nm, well consistent with the measured value of 0.7 nm. Thus it can be inferred that a high-quality APTS-SAM has been formed on the silicon substrate. On the other hand, the water contact angle on the APTS-SAM was measured to be about 49.6° (Table 1). Noticing that the contact angle for amino-terminated SAMs varies from 42° to 68° ,²⁵ and a high contact angle of APTS-SAM generally corresponds to a disordered structure due to the exposure of alkyl chains,²⁶ it can be deduced that the prepared APTS-SAM is well organized and most likely terminated with $-\text{NH}_2$. After being immersed in the TRIS-HCl solution of dopamine for 6 h, a 13.5-nm-thick layer of PDAc was deposited on the silicon substrate premodified by APTS-SAM. The water contact angle of the as-deposited film was measured to be 54.1° , quite close to the reported value of PDAc on the silicon wafer.²⁰ Upon the assembly of STC on APTS-PDAc, the thickness and water contact angle of the STC monolayer are measured to be about 2.1 nm and 97° ; both are smaller than the reported values of 2.6 nm and 110° for a fully covered STC monolayer.²⁴ The above analysis reveals that the STC monolayer is not packed densely enough and the STC molecules might be tilted on the PDAc surface, which is attributed to a low density of the amino groups on the PDAc surface or the incomplete derivatization of the amino groups by the STC molecules.

The ATR-FTIR spectra of the prepared samples on silicon wafers are shown in Figure 2. For APTS-SAM, the asymmetric and symmetric methylene vibrations located at 2928 and 2851 cm^{-1} are observed, respectively. The peaks at 1570 and 1460 cm^{-1} are assigned to the deformation vibration of N-H and C-H, respectively. The peak at 1376 cm^{-1} is assigned to the stretching vibration of the C-N bond. Upon the deposition of PDAc, 1450–1600 cm^{-1} typical signals of C-C vibration of benzene ring moiety in the dopamine molecule emerged. For the APTS-PDAc-C18 film, the characteristic bands at about 1645 and 1540 cm^{-1} assigned to amide I (predominantly C=O stretching) and amide II (involving torsional motion of both N-H and C-N) indicate that chemical reaction does occur between PDAc and STC, producing the amide group ($-\text{NHC}=\text{O}$), which is in agreement with those reported elsewhere.^{15,27–29} Moreover, the red shift of amide I (compared with $\sim 1690 \text{ cm}^{-1}$) and the blue shift of amide II (compared with $\sim 1510 \text{ cm}^{-1}$) bands are observed as compared with the ordinary state.^{15,28} The

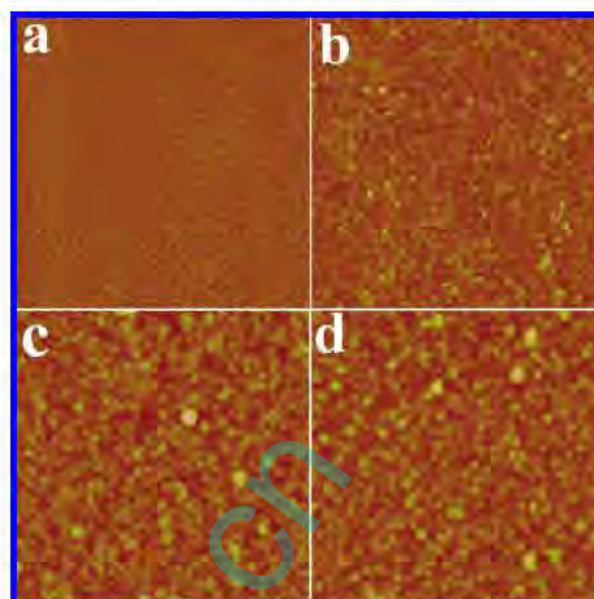


Figure 3. AFM morphologies of silicon substrate (a), APTS-SAM (b), APTS-PDAc (c), and APTS-PDAc-C18 (d) over a scanning area of $1 \mu\text{m} \times 1 \mu\text{m}$. For panels a and b, the Z range data scale is 5 nm, and for panels c and d, it is 20 nm.

band shift is caused by the hydrogen bonding, which can induce a decrease in the electron density of the C=O bond and an increased restriction in N-H bending. Whitesides²⁸ and Yang¹⁵ claimed the existence of hydrogen bonding in the SAMs based on the FTIR spectrum in which the amide I band was located at 1639–1650 cm^{-1} and the amide II at 1542–1550 cm^{-1} . Therefore, it is reasonable to conclude that hydrogen bonding exists authentically in the 3-layer thin film as indicated by the IR band shift.

To obtain precise information on the surface characteristics, surface morphology of the prepared samples was also observed by AFM. As shown in Figure 3, panels a and b, the surfaces of the silicon substrate and APTS-SAM are very smooth with the root-mean-square (rms) microroughnesses of about 0.20 and 0.30 nm over a scanning range of $1 \mu\text{m} \times 1 \mu\text{m}$, while, for samples of APTS-PDAc and APTS-PDAc-C18, the films are composed of plentiful regular grains (see Figure 3, panels c and d) and the surfaces are relatively rough with the rms microroughnesses of about 1.11 (APTS-PDAc) and 1.18 nm (APTS-PDAc-C18).

3.2. Adhesive and Microtribological Behaviors. Figure 4 presents the adhesion forces between the AFM tip and the sample surfaces. At 25% RH, strong adhesion of about 100 nN is observed on the hydroxylated silicon substrate. Once the dual-layer film of APTS-PDAc and the 3-layer film of APTS-PDAc-C18 are generated, the adhesion forces reduce to about 75 and 46 nN, respectively. The lowest value of 46 nN indicates that the APTS-PDAc-C18 film possesses the best adhesion-resistance performance. Moreover, the adhesion force is closely related to the water contact angle (as shown in Table 1), i.e., adhesion force greatly decreases with increasing hydrophobicity of the surface. Such variation is well understood since the adhesion mainly dominated by capillary force between the tip and the surface is dramatically lowered when the surface becomes highly hydrophobic.^{17–19}

The microtribological behavior of the fabricated films in air was evaluated with an AFM. In the measurements, the friction force is given as voltage signals, so it is infeasible to obtain the real friction coefficient. However, a relative friction coefficient

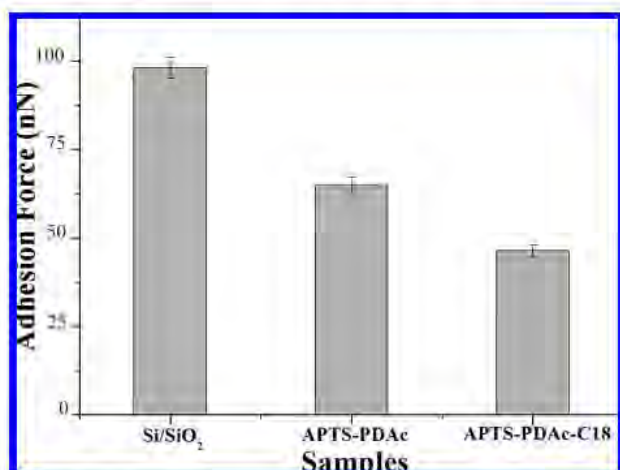


Figure 4. Adhesion forces between AFM tip and the surfaces of the Si/SiO₂, APTS-PDac dual-layer film, and APTS-PDac-C18 3-layer film (25% RH).

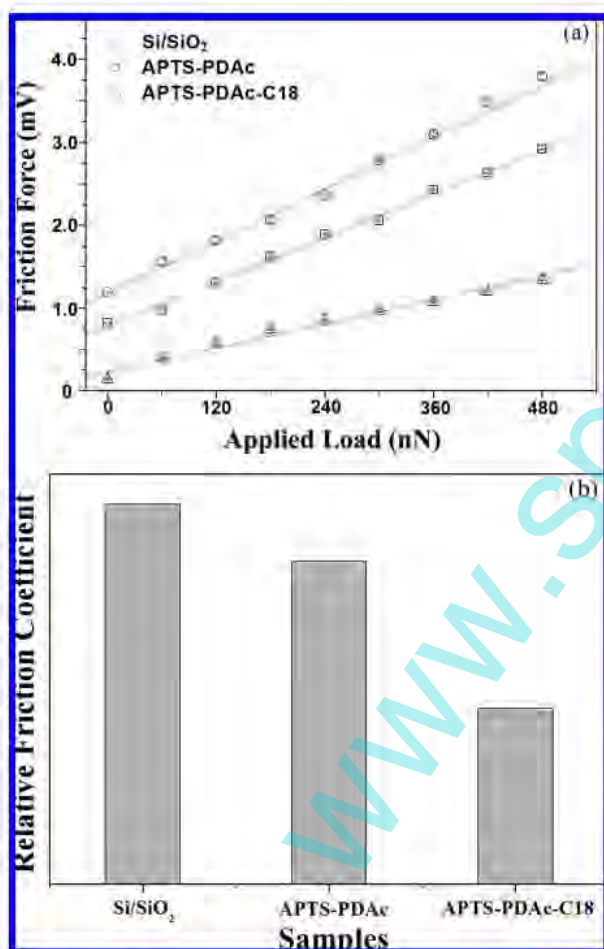


Figure 5. (a) Friction versus load curves for surfaces of bare silicon wafer, APTS-PDac, and APTS-PDac-C18 films; (b) relative friction coefficients directly derived from panel a

(RFC), the slope of the force curve, can be calculated since the voltage signals are proportional to the strength of the real forces.⁸ In this case, for a given AFM probe, the relative friction coefficients for various film samples can be compared among each other and the results are shown in Figure 5a. It can be seen that the profiles of friction force versus external load can be well fitted by Amontons' law:

$$F_L = \mu F_N + F_0$$

where μ is friction coefficient, F_L is the friction force, F_N is the normal load, and F_0 is the friction force at an external load of zero.^{8,30} The relative friction coefficients for various samples are summarized in Figure 5b. It is clearly obtained that both APTS-PDac and APTS-PDac-C18 reduce the friction force; especially, the 3-layer film of APTS-PDac-C18 exhibits much better lubricity. The excellent lubricity can be assigned to the hydrophobicity of the APTS-PDac-C18 film, which plays a significant role in reducing adhesion force between the tip and film surface. Many works have shown on a microscope that the friction would decrease with reducing adhesion.^{10,18,31,32} Besides, the low friction of the APTS-PDac-C18 also could be ascribed to the nature of the outer STC monolayer. Namely, the outer long chains have a significant freedom to swing and rearrange along the sliding direction under shear stress, and consequently yield a smaller resistance.¹⁸

3.3. Macrotribological Behavior. The wear-resistance ability is a key factor for organic films to be used as the boundary lubricants. The macrotribological behavior of the films was tested on a ball-on-plate macrotribometer under different conditions and the results were shown in Figure 6. As shown in Figure 6a, the APTS-PDac dual-layer film showed poor tribological properties characterized by high friction and very short antiwear life (the antiwear life refers to the sliding time at which the friction coefficient rises sharply, corresponding to lubrication failure of the film) under the conditions of 0.3 N and 1 Hz. After being modified with STC, the 3-layer film displayed greatly improved tribological properties, i.e., a lowered friction coefficient of about 0.20, and a lengthened antiwear life over 3600 s (Figure 6b). In our previous work, the dual-layer film of APTS-C18 was fabricated and the wear resistant performances were found to be excellent at a low applied load of 0.1 N,¹⁵ while in the present study, raising the applied load to 0.3 N, the APTS-C18 dual-layer film was easily destroyed in 50 s (Figure 6c).

Compared with the APTS-PDac dual-layer film, the remarkable decrease of the friction coefficient of the APTS-PDac-C18 3-layer film might be attributed to the high flexibility and low surface energy of the outer STC layer. Furthermore, in comparison with the dual-layer film of APTS-PDac or APTS-C18, the high wear-resistance and load-carrying capacities may result from the following two factors. First, as shown in Figure 1, interlayer combination of the multilayer film and the adhesion to silicon substrate are actualized all by chemical bonding, which, in association with the cross-linked interlayer of PDac, contributes to enhance the stability and load-carrying capacity of the film. Second, the STC monolayer possesses high elasticity and can endure larger stress, compression, and shear, without significant lateral displacement as have been reported by Houston and his colleagues.³³ In addition, the antiwear life of the APTS-PDac-C18 film is obviously decreased with increasing sliding rate (see Figure 6d) or load (see Figure 6e), which can be reasonably understood if one noticed that the higher load or shear velocity would intensify the oscillation and distortion of the organic molecules in the multilayer film leading to accelerated formation of defects and enhanced destruction of the film.

As demonstrated by many studies,^{34–37} the SAM may find potential application in the MEMs for its good friction reducing and antistiction performances. Distinctively, the present 3-layer film possesses much better load-carrying properties and may be more suitable for the relatively high load situations.

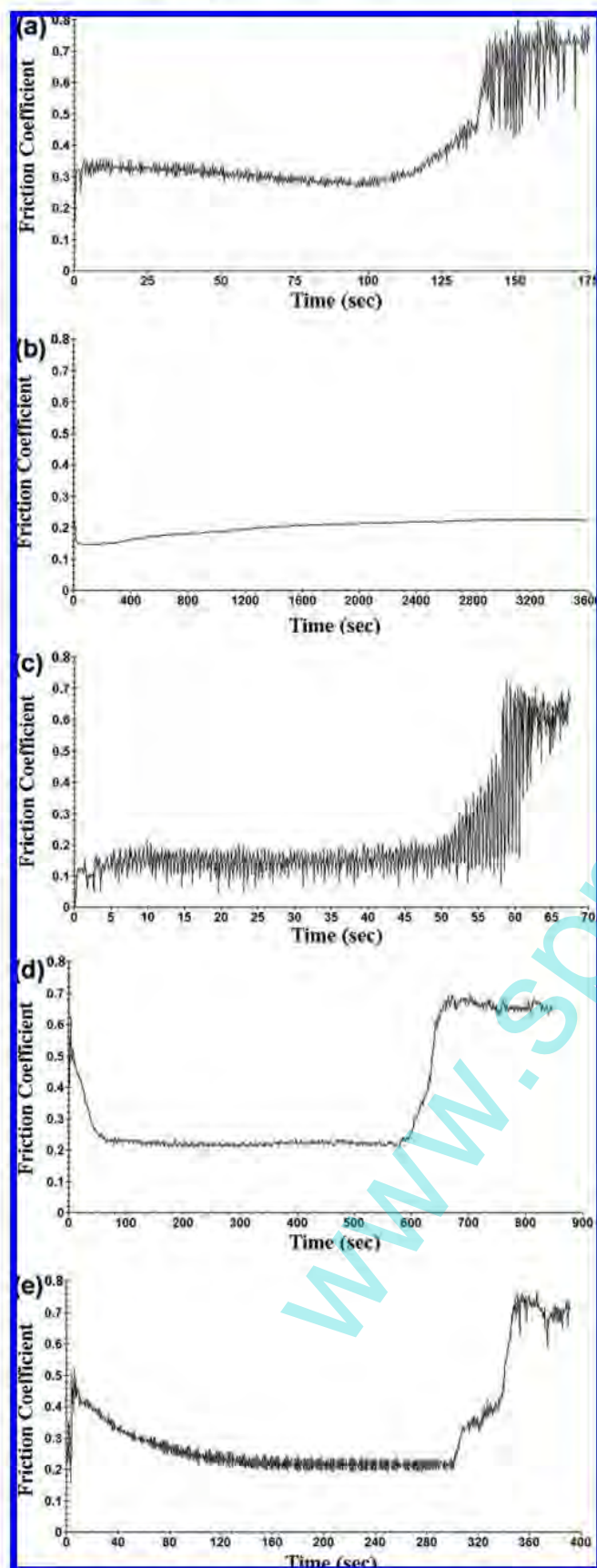


Figure 6. Variation in friction coefficient with time for various samples at different applied load and sliding frequency: (a) APTS-PDac, 0.3 N, 1 Hz; (b) APTS-PDac-C18, 0.3 N, 1 Hz; (c) APTS-C18, 0.3 N, 1 Hz; (d) APTS-PDac-C18, 0.3 N, 4 Hz; (e) APTS-PDac-C18, 0.5 N, 1 Hz.

4. Conclusions

A novel 3-layer organic film with PDac as the interlayer was constructed on a silicon surface via a multistep self-assembly route. The relationship between the tribological behavior and chemical structure of the film was studied. From the results, the following conclusions can be drawn:

(1) The interlayer combination of the 3-layer film and the adhesion to silicon substrate were actualized all by chemical bonding, which contributed to greatly enhance the stability of the film.

(2) Micro- and macrotribological studies showed that the outer STC layer played a significant role in decreasing the friction and increasing the antiwear ability of the 3-layer film, possibly due to its hydrophobicity, high flexibility, and high elasticity.

(3) The excellent antiwear ability of the 3-layer film was closely related to the special chemical structure. Namely, the strong adhesion to the silicon substrate, the chemical bonding between adjacent layers, the cross-linked structure of PDac, and the hydrophobicity and high elasticity of the outer STC layer jointly accounted for the greatly increased antiwear ability of the 3-layer film as compared with dual-layer films of APTS-PDac and APTS-C18.

(4) The antiwear life of the 3-layer film was closely related to the applied load and sliding velocity. Higher load and shear velocity would intensify the destruction of the film and shorten the antiwear life.

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