



Preparation and nano/microtribological properties of perfluorododecanoic acid (PFDA)–3-aminopropyltriethoxysilane (APS) self-assembled dual-layer film deposited on silicon

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ABSTRACT

Self-assembled dual-layer films have been expected to be excellent lubricants for micro/nano-electromechanical system (MEMS/NEMS). In this research, a novel self-assembled dual-layer film was prepared on single-crystal silicon surface by chemisorption of perfluorododecanoic acid (PFDA) molecules on 3-aminopropyltriethoxysilane (APS) self-assembled monolayer (SAM) with terminal amino group. The chemical composition, structure and morphology of the film were characterized by measurement of contact angle and thickness with ellipsometric method, and by the means of multi-functional X-ray photoelectron spectrometric (XPS) analysis, and atomic force microscopic (AFM) analysis. The nano- and microtribological properties of the dual-layer film were investigated. The dual-layer PFDA–APS film was hydrophobic with the contact angle for water to be about 105° and the overall thickness about 2.5 nm. Atomic force microscopic images revealed that the APS surface was initially characterized with uncontinuous asperities, the surface became relatively smooth and homogeneous after coating with PFDA film by SAM method. The PFDA–APS film exhibited low adhesion and it greatly reduced the friction force at both nano- and microscale. The film exhibited better anti-wear durability than the lauric acid (dodecanoic acid or LA)–APS self-assembled dual-layer film with same chain length and similar structure. PFDA self-assembled dual-layer film is intended for an application in the lubrication and protection of MEMS at low load.

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1. Introduction

The micro/nano-electromechanical systems (MEMS/NEMS) have obtained rapid development in the past decades due to their superior performance and low unit cost [1]. However, large surface area-to-volume ratio causes serious adhesive and frictional problems for MEMS operations [2]. Self-assembled monolayers (SAMs), formed typically by the adsorption of alkanethiols onto gold surfaces, or by the adsorption of alkylsilanes onto silica surface, have attracted widespread interest in a range of applications including fundamental studies of interfacial phenomena, such as wetting [3–5] and biological interaction [6], and development of novel functional molecular thin film architectures [7]. Recently, SAMs as ideal molecular lubricants for MEMS have been given great attention to solve the friction-related problems [8]. Alkylthiols, alkanolic acids and alkylsilanes, which are produced on gold and silicon surfaces,

respectively, are main popular systems to be used for this purpose [9–13]. However, finding optimum lubricants for the MEMS continues to be a challenge in nanotribology field. Investigation about the tribological behavior of SAMs derived from alkylsilanes has been an active topic and it is imperative to find better lubricants for MEMS with longer durability and better tribological performance [14–16].

SAMs have good rupture properties due to their strong bonding to the substrate surface; they are expected not to freely migrate on the surface. However, some molecules from SAMs may transfer to the surface of counterpart when external force was applied on the contacting surface [17]. Because of monolayer structure and flexibility, SAMs exhibit poor anti-wear durability [18–20]. To utilize SAMs as lubricants to protect MEMS, it is necessary to consider the molecule layer structure as well as the strongly bonded characteristics of lubricant [21]. To minimize interfacial energy, SAMs with low surface energy (e.g., perfluorinated *n*-alkanoic acid, C_nH_{2n-1}O₂H) are applied on the surfaces of the digital micromirror devices (DMD), which are used to reduce stiction during contact between the spring tip and the landing site [22]. Our previous results [23,24] indicated that the dual-layer structure can help to

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improve the film quality, reduce the friction coefficient and significantly enhance their durability and load-carrying capacity. We intended to design a lubrication system consisting of a dual-layer SAM film with terminal group to minimize adhesive force and with an appropriate molecular structure to prolong durability.

This work aims to further improve the micro/nanotribological behavior of the SAMs and to acquire insights into their potential in resolving the tribological problems of MEMS/NEMS. A self-assembled dual-layer film was prepared, using the chemisorption of the perfluorododecanoic acid (PFDA) molecules on APS-coated single-crystal silicon surface. The micro- and nanotribological properties of the developed dual-layer film, single APS self-assembled monolayer, and lauric acid (LA)–APS self-assembled dual-layer film were evaluated and compared.

2. Experimental

2.1. Materials

Polished and cleaned single-crystal silicon (100) wafers, obtained from GRINM Semiconductor Materials Co., Ltd., Beijing, were used as substrate. The roughness of the wafer used was 0.45 nm. 3-Aminopropyltriethoxysilane (APS, 99%) was obtained from ACROS (NJ, USA). Perfluorododecanoic acid (PFDA, 98%) was purchased from ABCR GmbH & Co., KG and used as received. Lauric acid (LA, 98%; Hushi Chemical Co., Ltd., Shanghai) and toluene (99.5%, anhydrous; Gaofeng Chemical Co., Ltd., Tianjin) were used as received.

2.2. Preparation of self-assembled films

Silicon wafers were cleaned and hydroxylated by immersing in piranha solution (a mixture of 7:3 (v/v) 98% H₂SO₄ and 30% H₂O₂) at 90 °C for 30 min. The wafers were then fully rinsed with ultra-pure water, placed into the APS solution of 5.0 × 10⁻³ M in a mixed solvent of acetone and ultra-pure water (v/v=5:1), and held for 24 h. The target monolayer of APS was thus formed on the hydroxylated silicon substrates. After rinsing with ultra-pure water, the APS-coated silicon substrate were put into a dilute solution of 1.0 × 10⁻³ M PFDA in dehydrated toluene at 80 °C and kept for 1 h. The coated films were annealed at 185 °C in nitrogen for 30 min to accelerate the acidamide reaction between PFDA and APS, then cooled in a desiccator. A monolayer of PFDA was presumably produced on the top of the APS film since the terminal amino groups in APS can react with carboxyl groups in PFDA to form chemical bonds. The developed dual-layer film samples were washed ultrasonically with toluene, acetone and deionised water in turn to remove the other physisorbed ions and molecules. The LA–APS self-assembled dual-layer film was prepared in the same way.

2.3. Characterization of the films

The static contact angles for ultra-pure water on the films were measured with Kyowa contact angle measurement apparatus. At least five replicate measurements were carried out for each specimen and the measurement error was below 2°.

The thickness of the films was measured on a Gaertner L116-E ellipsometer, which was equipped with a He–Ne laser (632.8 nm) set at an incident angle of 50°. A real refractive index of 1.40 was assumed for all the films. Five replicate measurements were carried out for each specimen and the thickness was recorded to be an accuracy of ±0.3 nm.

Chemical compositions and structures of the surface were examined with a PHI-5702 multi-functional X-ray photoelectron spectrometer (XPS), using a pass energy of 29.35 eV, an excitation

source of Mg K α radiation ($h\nu = 1253.6$ eV) and take-off angle of 35°. The chamber pressure was about 3 × 10⁻⁸ Torr under tested condition. Peak deconvolution and quantification of elements was accomplished using the software and sensitivity factors supplied by manufacturer. The binding energy of adventitious carbon (C_{1s}: 284.8 eV) was used as a basic reference.

A CSPM4000 atomic force microscope (AFM) with tapping mode was used to observe the film morphology.

The nanotribological behavior of the dual-layer film was characterized with an AFM/FFM controlled by CSPM4000 electronics, using the contact mode. Commercially available rectangle Si₃N₄ cantilevers with a normal force constant, 0.4 N/m, a radius of less than 10 nm and backside coated by gold (Budgetsensors Instruments Inc.) was employed. The force–distance curves were recorded and the pull off force reckoned as the adhesive force was given by

$$F = K_c Z_p$$

where K_c is the force constant of cantilever and Z_p is the vertical displacement of the piezotube, i.e., the deflection of the cantilever [25,26].

The friction force is a lateral force exerted on a tip during scanning and can be measured using the twist of the tip/cantilever assembly. To obtain friction data, the tip was scanned back-and-forth in the x-direction in contact with sample at a constant load while the lateral deflection of the lever was measured. The differences in the lateral deflection or friction signal between back-and-forth motions is proportional to the friction force. The friction force was calibrated by the method described in Ref. [27]. Friction forces were continuously measured with various external loads. The load was increased (or decreased) linearly in each successive scan line and typically normal loads ranged from 0 to 100 nN. Scanning for the friction force measurement was performed at a rate of 1 Hz along the scan axis and a scan size of 1 μm × 1 μm (viz. sliding velocity of 2 μm/s). The scan axis was perpendicular to the longitudinal direction of the cantilever. The sets of data were displayed graphically in a friction image.

The microtribological behavior of the dual-layer film was characterized with a ball-on-inclined plane micro-tribometer. Ball-on-inclined plane test apparatus was first developed at National Institute of Standards and Technology (NIST) [28,29,21], and the main idea of the test is to measure the shear rupture strength and durability of several nanometer films on surfaces of nanometer scale roughness. The sample was fixed on an inclined sample holder and the angle of inclined plane was adjusted to 0.035°. A stainless steel ball with diameter of 3.18 mm was used to impact the film during reciprocal sliding. High-precision semi-conductor strain gauges were used to measure the friction force and applied load continuously; the load was fixed to 10 mN during the test and it was dynamically adjusted to maintain the same value. All the test was done in a class-10 clean room at humidity of 15% RH and temperature of 20 °C.

The worn surfaces of the films were observed on a MicroXAM 3D non-contact profilometer (ADE Phase Shift Inc., USA) with phase mode.

3. Results and discussion

3.1. Structure and morphology characterization

The measurement of static contact angle is an effective way to reflect the variation of the chemical composition of solid surfaces. The contact angles for water on the hydroxylated silicon surface and the self-assembled films are shown in Table 1. Natu-

Table 1
Contact angle and thickness for the silica layer and the modified silicon surfaces

Test samples	Water contact angle (°)	Thickness (nm)
SiO ₂ /Si	~0	~1.8
APS	44.0	0.5
PFDA	105.0	2.0

rally, the hydroxylated silicon surface and the APS monolayer are hydrophilic, with the water contact angles about 0° and 44.0°, respectively, which agree well with what have been reported [30,31]. Once the PFDA layer was chemically adsorbed onto the APS monolayer, the contact angle greatly increased to 105° and the resulting dual-layer film surface become hydrophobic. The results of thickness ellipsometric measurement are also listed in Table 1. After hydroxylating in the piranha solution at 90 °C for 30 min, a silica layer of about 1.8 nm thickness was generated on the silicon wafer. The film for single APS and PFDA layer was about 0.5 and 2.0 nm in thickness, respectively. The variation of contact angles and the thickness indicates that the PFDA molecules have successfully adsorbed onto the APS-coated silicon surface. The APS monolayer with terminal amino group is ready to make the acidamide reaction with the carboxylic acid at 185 °C in nitrogen. On the basis of the covalent amide bond between the PFDA and APS molecules, the reaction process is schematically shown in Fig. 1.

The surface chemical composition and structure of PFDA–APS self-assembled dual-layer film was determined by XPS. The procedure involved the measurement of the C 1s, N 1s, and F 1s core level spectra for surfaces of these films. Fig. 2 displays the spectra obtained from the APS film before and after reaction with perfluorododecanoic acid. While a single high symmetrical peak of 688.4 eV appeared in the F 1s spectrum as shown in Fig. 2a and three peaks of 398.7, 399.8 and 400.7 eV were observed in N 1s spectrum as shown in Fig. 2b, there are four new peaks arising from C 1s (Fig. 2c), compared with C 1s (Fig. 2d), before treat-

ment with PFDA. The first new peak at 286.1 eV might originate from the C atoms bonded to the N atoms (O=C–N–C*) [32], while the second new peak at 288.1 eV can be assigned to the carboxyl C atoms (O=C*–N–C) [32]. The third and fourth new peaks at 291.3 and 293.5 eV can be attributed to the CF₂ and CF₃ group in PFDA, respectively [32]. The fitting results present the surface elemental and functional group composition, as well as, some ratios of element and functional group quantities, such as –CF₂– and –CF₃. The ratio of the peak areas for the –CF₂– and –CF₃ functional groups is 9.3, which approach an expected value of 10 based upon the chemical formula for PFDA. Above assignments clearly indicate the chemical reaction between PFDA and APS. The spectrum for N 1s spectra shown in Fig. 2b further supports this conclusion. While the peak at 399.8 eV is assigned to the N atoms in amine group, the peak appearing at 400.7 eV can be attributed to the N atom bonded to carbonyl group (O=C–N*) [32–34]. Formation of carbonyl group resulted in 0.9 eV chemical shift. Chance and Purdy [31] got similar results. As to the peak at 398.7 eV, it might come from free aliphatic amines in APS [35].

AFM morphological images of APS monolayer and PFDA–APS dual-layer films are presented in Fig. 3. Some lubricant film aggregated somewhere are seen on the APS surface in Fig. 3a, which might come from the silicon surface itself or the polymerization of APS in solution and unevenly deposited onto the silicon wafers surface. After formation of the PFDA layer, the film surface became relatively smooth and homogeneous as shown in Fig. 3b. The microroughness in root-mean-square (RMS) of the monolayer was estimated to be 0.408 nm over an area of 1 μm × 1 μm, which is a little bit lower than the 0.447 nm of the APS monolayer surface. These observations indicate that the adsorption of the PFDA molecules onto the APS helps to reduce roughness of surface and improve the film quality.

3.2. Nanotribological behavior

The adhesive forces between the AFM tip and the film surfaces are shown in Fig. 4. Strong adhesion was observed on the silicon surface at relative humidity of 15%, on which the adhesive force was about 14 nN. After PFDA–APS dual film was generated, the adhesive force was decreased to 7 nN. This indicates that the PFDA–APS dual-layer film exhibited low adhesion due to fluorinated carbons. It is also observed that the adhesive forces are closely related to the contact angles as shown in Table 1. In other words, the adhesive force is greatly decreased with increasing hydrophobicity of the surface. Such phenomenon indicates that PFDA–APS dual film on the silicon surface can obviously lower interfacial energy on silicon wafers and the capillary force between the tip and surface.

Fig. 5 presents the plot of friction versus load curves for the hydroxylated silicon surface, APS monolayer and PFDA–APS dual-layer film measured using a gold-coated Si₃N₄ tip. Both the films greatly reduced the friction force, and especially the PFDA–APS dual-layer film exhibited much lower friction coefficient. This is because the long chains of the PFDA molecules with one end attached to substrate surface have a significant freedom to swing and rearrange along the sliding direction under shear stress, and long chain molecules caused the further orientation under the normal load applied by AFM tip. The orientation of the molecular springs reduced the shearing force at the interface, which in turn reduced the friction force. In elasticity deformation range, when the tip slips away, the orientated and compressed molecules may almost recover to their initial state [36,37]. Furthermore, the low friction of the PFDA–APS dual-layer film could also be attributed to the lower interfacial energy. Thus, the results highly suggested that the PFDA–APS dual-layer film can greatly reduce the adhesive force and friction on silicon surface.

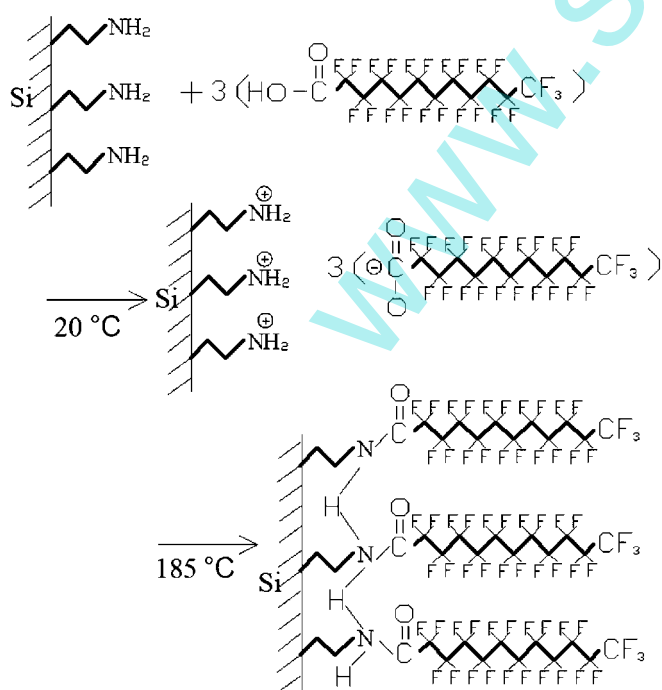


Fig. 1. Schematic structure and forming process of PFDA molecules chemically adsorbing onto APS monolayer surface.

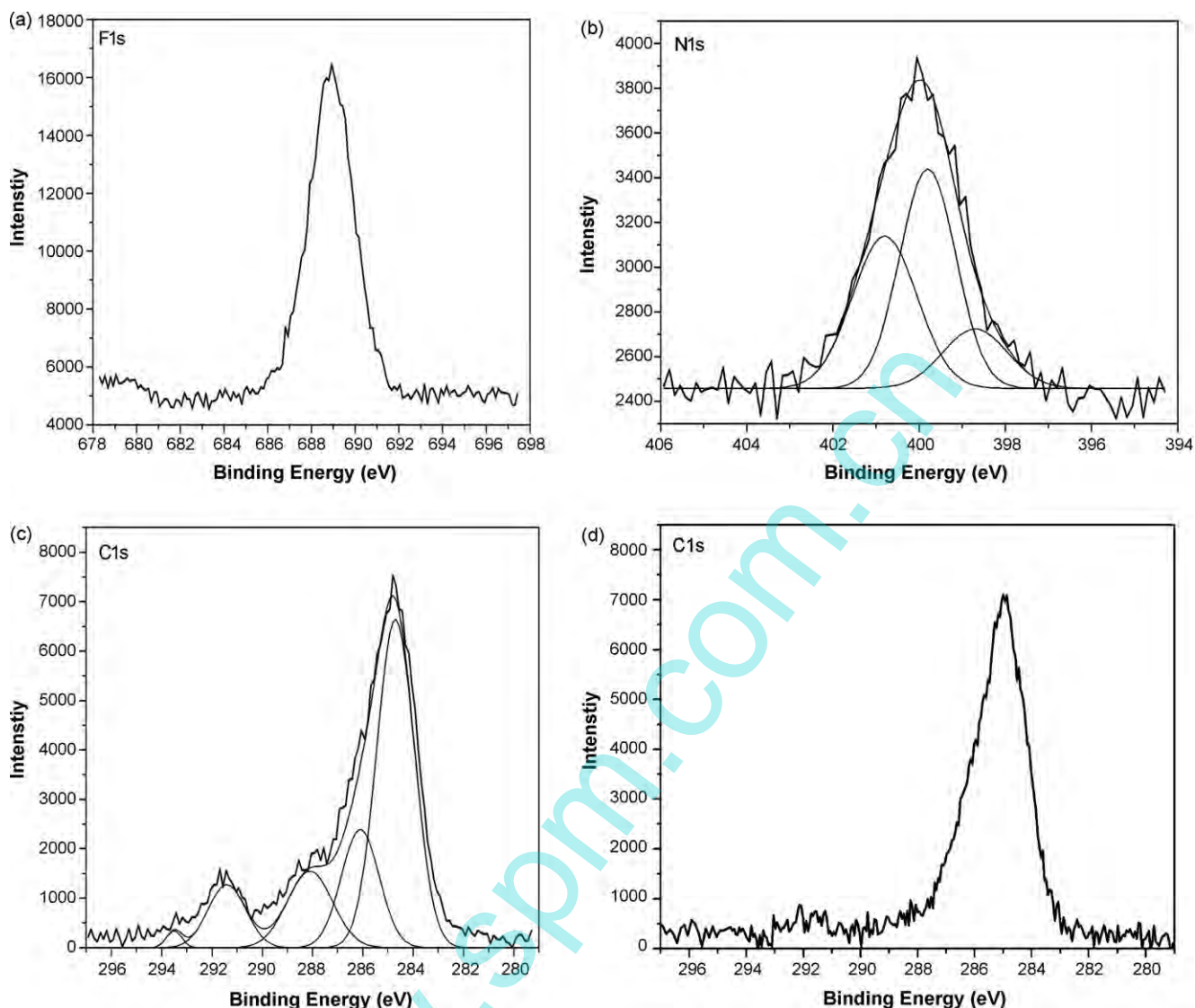


Fig. 2. XPS spectra of APS film (a–c) after and (d) before reaction with perfluorododecanoic acid.

3.3. Microtribological behavior

Fig. 6 shows friction force and coefficient of the PFDA–APS dual-layer film, LA–APS dual-layer film and APS monolayer. As shown in Fig. 6a, the friction force of APS monolayer, PFDA–APS dual-layer film and LA–APS dual-layer film increased with increasing external linear loads. It is observed that both PFDA and LA dual-layer films exhibited lower values of friction force than the APS monolayer in the testing range of the loads tested, and the friction force of LA dual-layer film is a little bit lower than that of PFDA. Fig. 6b shows the variation of friction coefficient as a function of sliding cycles at applied normal load of 10 mN and sliding speed of 0.2 mm/s. It can be seen that PFDA–APS and LA–APS dual-layer films exhibited low initial friction coefficient of about 0.16 and 0.07, respectively. It is also observed that the durability of PFDA–APS dual-layer film exceeded 1000 sliding cycles with a stable and low friction coefficient value (0.17). The friction coefficient of LA–APS dual-layer film raised to a stable and low value (0.11) at about 600 sliding cycles, and increase abruptly to the high value (0.65) at about 900 sliding cycles. Unlike the corresponding AFM/FFM results shown in Fig. 5, APS monolayer exhibited poor lubrication at micro scale. A friction

coefficient about 0.6 is observed after first sliding cycle, which is the same as that of the silicon surface. It is supposed that the large difference anti-wear durability of dual-layer film and APS monolayer possibly resulted from their different structure. Namely, the PFDA–APS and LA–APS dual-layer films have a two-layer structure of which the defects of APS monolayer film can be compensated by layered structure [14]. At the same time, the mechanical stability of these dual-layer films can be enhanced by the Van der waals attractive force of the F–F or H–H between nearest neighbor backbone chains, as shown in Fig. 1, which are not available in APS monolayer. The different friction behavior of these dual-layer films may be due to that PFDA film has stronger F–F Van der waals attractive force between nearest neighbor CF_2 backbone chains within PFDA film than that of H–H within LA film. In other word, the CF_2 backbone chains provided a more densely packed arrangement than hydrocarbon chains resulting in the fluorocarbon monolayer stiffer than their hydrocarbon counterparts [38]. Between monolayers with fluorocarbon and hydrocarbon backbone chains, the stiffness of the fluorocarbon backbone chains as compared to the hydrocarbon backbone chains result in the higher friction for PFDA than LA [39,40]. Furthermore, the weak intermolecular chain–chain inter-

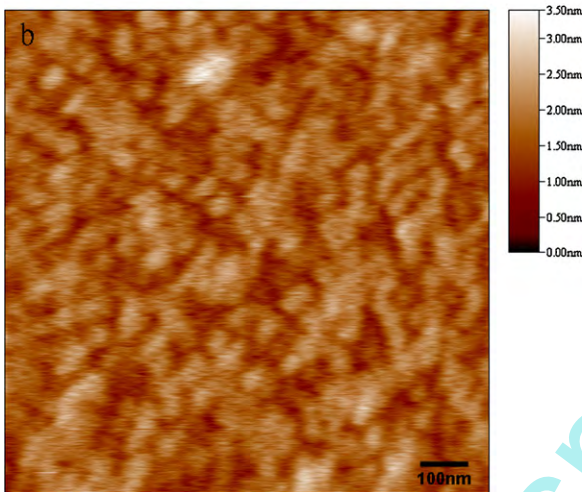
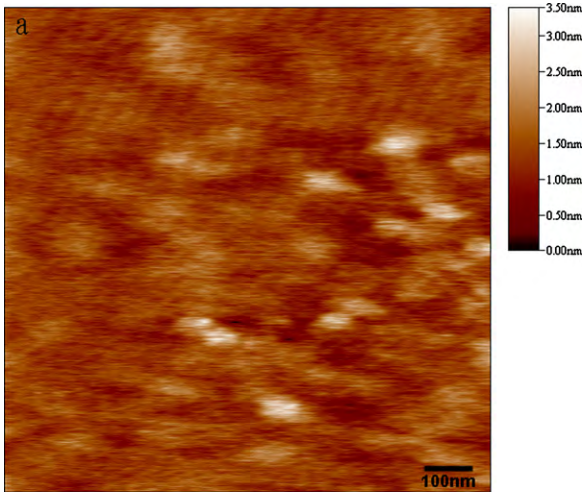


Fig. 3. AFM topographic images of APS monolayer (a) and PFDA-APS dual-layer film (b) on silicon wafer.

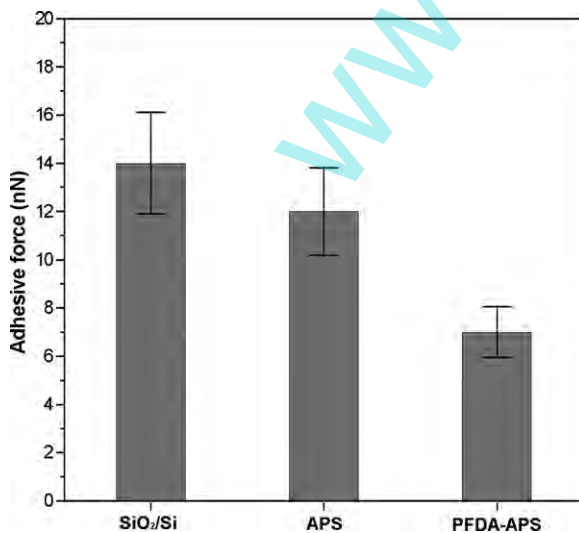


Fig. 4. Adhesion forces between AFM tip and the surfaces of the SiO₂/Si, APS monolayer and PFDA-APS dual-layer film at a scanning velocity of 1 μm/s (15% RH).

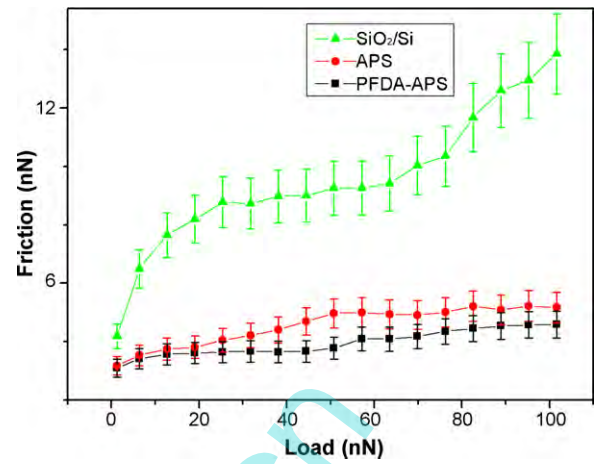


Fig. 5. Plot of friction and load for surfaces of the SiO₂/Si, APS monolayer and PFDA-APS dual-layer film at a scanning velocity of 1 μm/s (15% RH).

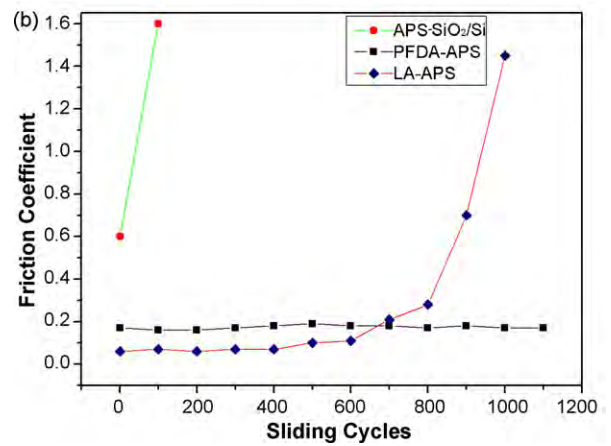
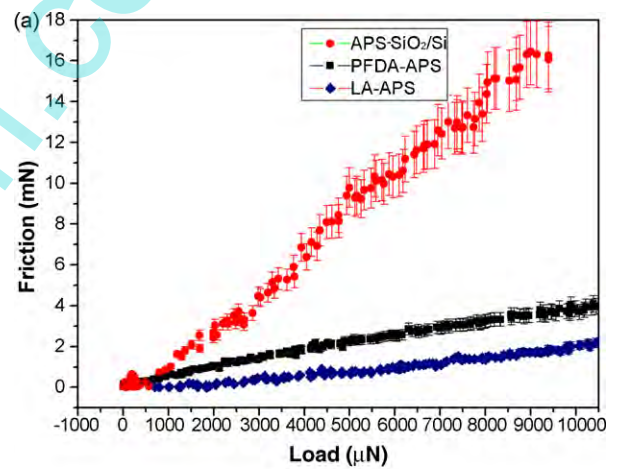


Fig. 6. Microtribological behaviors of the APS monolayer, PFDA-APS dual-layer film and LA-APS dual-layer film surfaces sliding against a steel ball: (a) friction versus load curves for surfaces of these films (15% RH) and (b) variation in the friction coefficients with sliding cycles for these films at a normal load of 10 mN and a sliding speed velocity of 0.2 mm/s.

action can make hydrocarbon backbone chains freely rotate around, which lead to poor anti-wear durability even though it exhibited low friction coefficient at initial stage.

To further clarify the role of the PFDA film and dual-layer structure in exhibiting worn surfaces of the silicon wafer, LA-APS and PFDA-APS dual-layer films after sliding against steel ball at same condition of applied normal load of 10 mN and sliding speed

velocity of 0.2 mm/s, the morphologies of the worn surfaces were observed on a 3D non-contact profilometer which has nanometer scale resolution in height direction as shown in Fig. 7. The APS monolayer worn surface is characterized by severe plastic deformations and fractures even after 200 sliding cycles in Fig. 7a. With the LA-APS dual-layer film on the silicon surface, the scratch was observed on the worn surface and there were shallow grooves on the surface after 1000 sliding cycles in Fig. 7b. As shown in Fig. 7c, when the PFDA molecules was chemisorbed on the APS monolayer, the wear of surface was significantly reduced, and the scratch was nearly indistinguishable and the scratch depth was less than several nanometers. It means that the PFDA film successfully prevented the wear of materials. The worn surface morphologies agreed well with the corresponding tribological properties that the PFDA-APS dual-layer film exhibited better wear resistance and longer durability than single APS monolayer and LA-APS film.

4. Summary and conclusions

This work has demonstrated that a novel self-assembled dual-layer film was prepared by chemisorption of the PFDA molecules onto the self-assembled monolayer of APS with terminal amino group on single-crystal silicon surface and the dual-layer film overall thickness about 2.5 nm. Nano/microtribological behavior of the PFDA-APS dual-layer film was investigated and the film was compared with a single APS monolayer and the dodecanoic acid or LA-APS film. The PFDA self-assembled dual-layer film exhibits better adhesive resistance and lower friction coefficient than single APS monolayer in nano- and microscales. Furthermore, it exhibited better anti-wear durability compared with LA-APS dual-layer film and single APS monolayer in micro scale. Thus, the PFDA self-assembled dual-layer film is intended for an application in the lubrication and protection of MEMS at low load.

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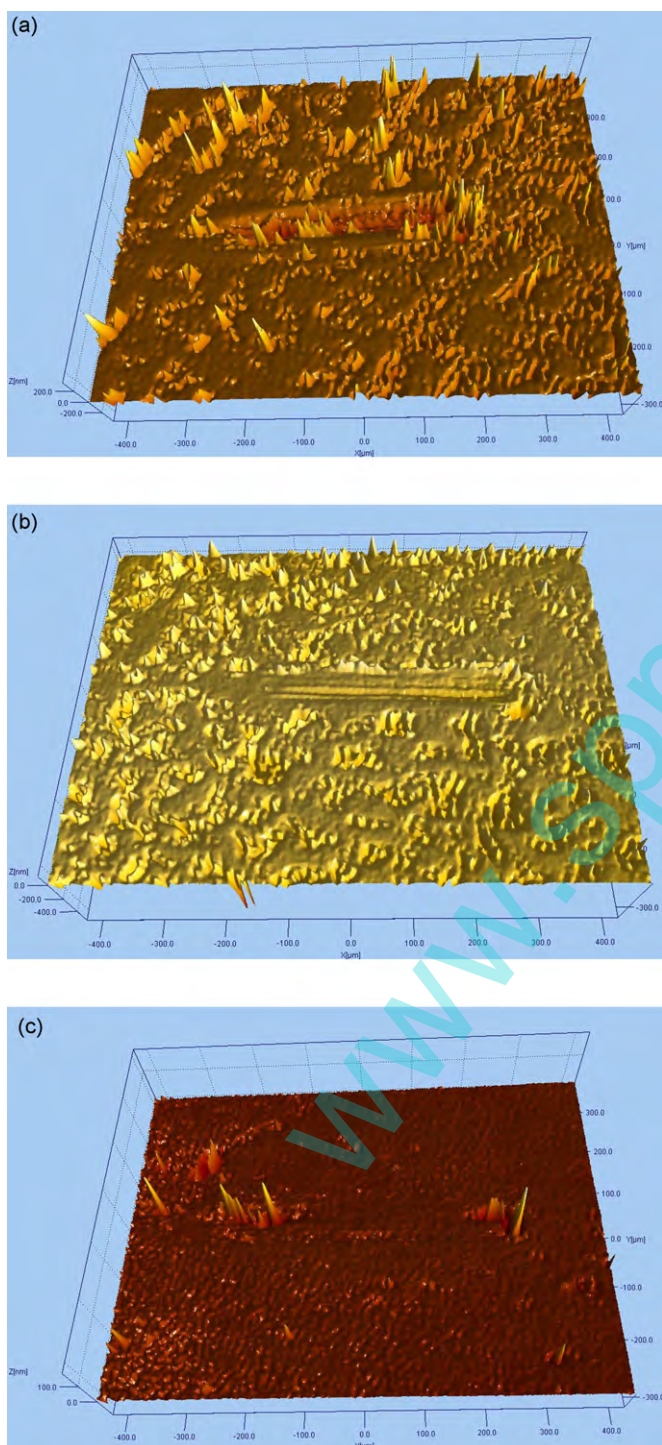


Fig. 7. 3D non-contact profilometer images of the worn surfaces of the APS monolayer, LA-APS dual-layer film and PFDA-APS dual-layer film samples sliding against steel ball at the same normal load of 10 mN and different sliding cycles: (a) the APS monolayer sliding for 200 cycles, (b) the LA-APS dual-layer film sliding for 1000 cycles, and (c) the PFDA-APS dual-layer film sliding for 1000 cycles.

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