Research Article

Micro/macrotribological properties of several nano-scale ionic liquid films on modified silicon wafers

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Three kinds of alkylimidazolium base room temperature ionic liquids (RTILs) were synthesized and their nano-scale lubricant films were prepared on modified silicon wafers by dip-coating method. The thicknesses of these films were measured and their relationship between thickness and solution concentration was obtained. Their surface morphologies were observed and contact angles of water on these films were determined. The adhesions and friction coefficients of these films were detected by contact mode AFM. As comparison, their macrotribological properties were evaluated on a UMT-2MT tribo-tester. It was found that, in microscale, 1-hexyl-3-methyl-imidazolium hexafluorophosphate performed the best tribological properties, while in macroscale, its tribological properties were similar with that of 1-hexyl-3-methyl-imidazolium tetrafluoroborate and better than that of 1-hexyl-3-methyl-imidazolium adipate. Copyright © 2009 John Wiley & Sons, Ltd.

Keywords: ionic liquids; ultra-thin film; adhesion; tribology

Introduction

As a kind of novel material, ionic liquids have many unique properties, such as negligible volatility at a relatively high temperature, nonflammability, high thermal stability, etc.[1] These characteristics have attracted great attention and made them available in many potential applications, for example catalysis, electrochemistry, separation science for extraction of heavy metal ions, as solvents for green chemistry, and materials for optoelectronic applications.[2–5] The above-mentioned properties of ionic liquids also make them excellent lubricants. Ye et al.[6] investigated the tribological behavior of two kinds of alkylimidazolium tetrafluoroborate and found them versatile lubricants for the contacts of steel/steel, steel/aluminum, steel/copper, steel/SiO_2, Si_3N_4/SiO_2, steel/Si (100), and steel/sialon ceramics. Other studies[7–10] investigated the tribological properties of other alkylimidazolium base ionic liquids and proved that they are superior to traditional lubricants such as phosphazene (X-1P), perfluoropolyether (PFPE), and zinc dialkyldithiophosphorate (ZDDP), in terms of antiwear performance and load-carrying capacity. Bermúdez et al.[11–13] discovered that some ionic liquid additives had better lubricating and antiwear properties than neat ionic liquids in aluminum/steel contact.

As lubricant film, ionic liquids also exhibit good tribological properties. Yu et al.[14] prepared two kinds of ionic liquid films with thickness of about 30 nm on modified Si surfaces and investigated their tribological properties on a dynamic/static friction coefficient measurement apparatus with PFPE as a comparison. They found that the ionic liquid exhibited better friction-reducing and antiwear abilities than the Zdol-2000 film. They attributed the excellent tribological properties of these ionic liquid films to their strong adsorptions to the interface and the good transfer film-forming abilities on the counterpart surfaces.

Recently, great developments have been achieved in microelectromechanical devices (MEMs), microsystems, nanotechnology, nanoelectromechanical devices (NEMs), etc. The spacing between surfaces in such devices is often separated by only nanometers.[15]

Therefore lubricant films with thickness of nanometers would be more suitable to present applications. We have studied the effect of anion on the tribological properties of ionic liquid films with a thickness of 2 nm on surface-modified silicon wafers in macroscale,[16] and we found that it was the mobility, rather than chemical change, that decided the macrotribological properties of ionic liquid films.

In this paper, three kinds of ionic liquid films with thickness of about 4 nm were prepared and their micro- and macrotribological properties were investigated and their distinctions were also discussed.

Experimental

Materials

(3-Aminopropyl)trimethoxysilane (APS, produced by Aldrich Chemical Company, purity ≥ 97%) was a commercial product and used directly. Three kinds of ionic liquids, 1-hexyl-3-methyl-imidazolium tetrafluoroborate (denoted as IL106B), 1-hexyl-3-methyl-imidazolium hexafluorophosphate (denoted as IL106P) and 1-hexyl-3-methyl-imidazolium adipate (denoted as IL106A) were prepared according to the literature[1] and characterized by means of ^{1}H nuclear magnetic resonance (NMR) spectroscopy with acetone-d_6 as solvent. Figure 1 shows the chemical formulations of these ionic liquids. All the other reagents of analytical grade were used as received.

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Figure 1. Chemical formulations of three kinds of ionic liquids.
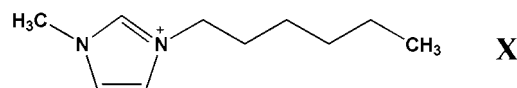
IL106B: $X=BF_4^-$

IL106P: $X=PF_6^-$

IL106A: $X=\bar{\ }OOC(CH_2)_4COO^-$

Pretreatment of silicon wafers

Cleaned silicon wafers were immersed in Piranha solution (volume ratio 7 : 3 of 98% H_2SO_4 and 30% H_2O_2) at 90 °C for 40 min to get a hydroxyl-terminated surface.[17] The hydroxylated Si wafer was immersed in 5 mmol/l APS/acetone solution for 24 h to obtain an amino-terminated surface.[18] Two kinds of surfaces described above were rinsed three times with distilled water, and then dried in fast nitrogen flow.

Figure 2 shows the schematic diagram of above process.

Film preparation

Ionic liquids of 0.1%, 0.2%, 0.3%, 0.4%, and 0.5% (wt.%) were dissolved in acetone, respectively. The corresponding films were prepared on the two kinds of modified substrates mentioned above with dip-coating method in class-100 clean room. The thicknesses of these films were measured by L116-C ellipsometer (Gaertner, USA) equipped with a He–Ne laser ($\lambda = 632.8$ nm) at a fixed incidence angle of 50°. Figure 3 shows the relationship between the concentration of IL106A and the thickness of its film on hydroxyl-terminated surface. It could be seen that the film thickness is in proportion to the concentration of the ionic liquid solution. It should be pointed that the thickness of other two ionic liquids of IL106B and IL106P were also in proportion to their corresponding solution if their concentrations were appropriate, for example lower than 1.0%, though the figures were not shown here. According to this relationship, three kinds of ionic liquid films with a thickness of about 4 nm were easily prepared.

Ionic liquid films' characterization

The static contact angles of distilled water on various surfaces were measured on a DSA100 Drop Shape Analysis System (Krüss
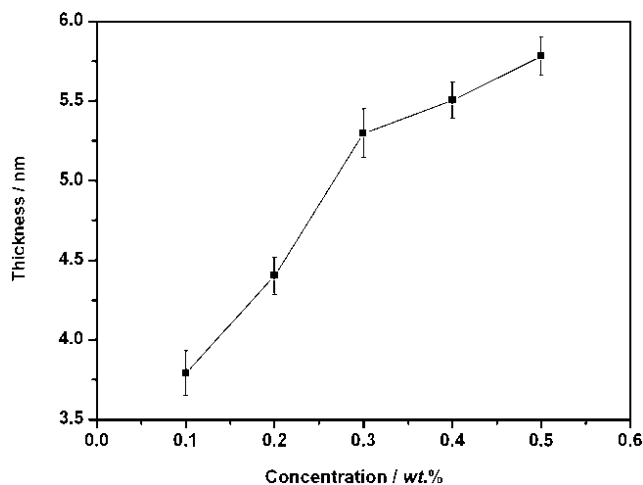

Figure 3. Relationship between the concentration of IL106A and the thickness of its film on hydroxyl-terminated surface.

GmbH, German). Five repetitive measurements were operated at different regions of the same film surface and averaged contact angles were obtained.

The film morphology was observed on a CSPM-4000 atomic force microscopy (AFM, Being Nano-Instruments Ltd., China) using tapping mode.

AFM was also employed to measure the adhesion and microfriction coefficient of these films using contact mode. Square pyramidal Si_3N_4 tips with a nominal less than 10 nm radius mounted on Al-coated triangular Si_3N_4 cantilevers with spring constants of 2.0 N/m were used. Adhesions were calculated from the force distance curves. Friction forces were obtained from friction loops at 10 separate points on each surface with a scan velocity of 2 µm/s. For all measurements, the same cantilever was used. Experiments were carried out under ambient conditions of 20–25 °C and 30–40% relative humidity. Because the voltage signal should be proportional to the real friction force,[19,20] the output voltages were directly used as friction forces and were defined as relative friction force. Therefore, the friction forces on various film surfaces can be compared with one another when the same AFM tip is used. Accordingly, the ratio of voltage to applied load was defined as relative friction coefficient in this paper.
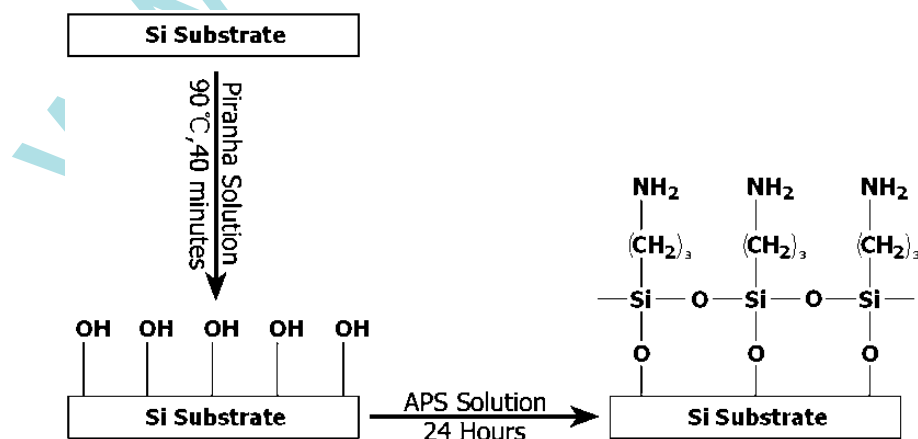

Figure 2. Schematic diagram of surface pretreatments.

Macrotribological properties of these films were evaluated on a UMT-2MT tribo-meter (CETR, USA) with a reciprocating-sliding mode. The reciprocating distance was 5 mm, and the reciprocating times per second were defined as frequency. The friction coefficient was recorded with computer and the lifetime of film was defined as the sliding time when the friction coefficient sharply increased to 0.6. A standard AISI-52 100 steel ball of 3 mm in diameter was selected as counterpart. The root mean square (RMS) roughness of the ball employed was about 50 nm.

Table 1. Contact angles (°) of modified Si surfaces and ionic liquid films on them

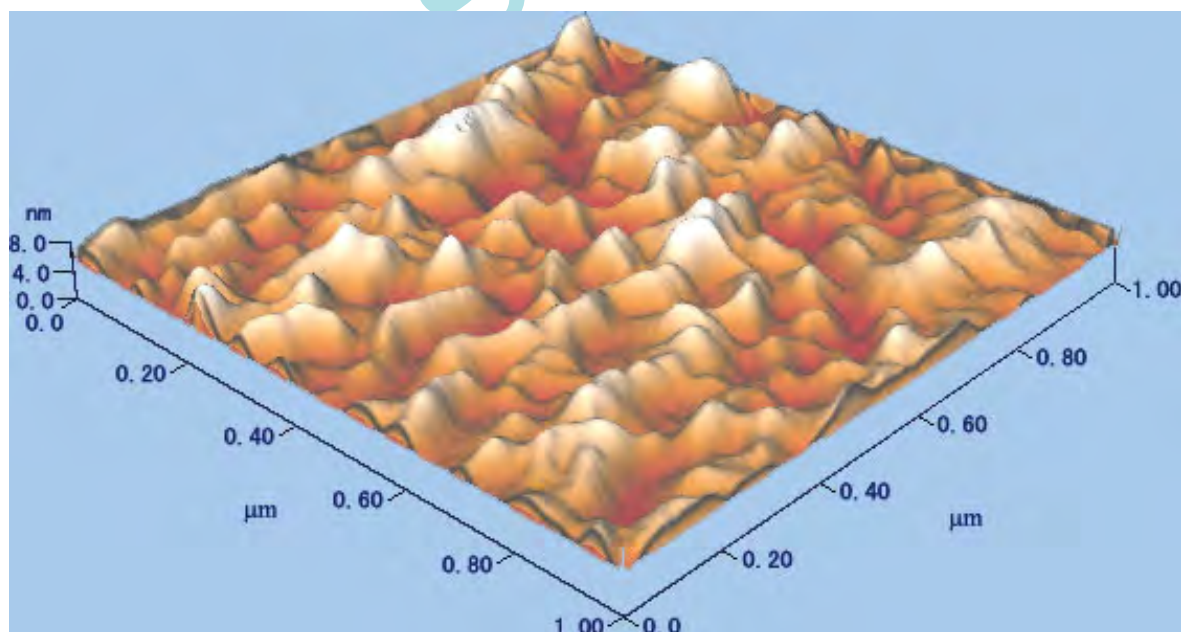| Surface	Hydroxyl-terminated Si	Amino-terminated Si
No IL Film	<5	59
Coated With IL106B	23	24
Coated With IL106A	19	22
Coated With IL106P	68	71

Results and Discussion

Characterizations of ionic liquid films

Figure 4 shows the morphology of ionic liquid film observed on tapping-mode AFM. It could be seen from the image that the film was uniformly prepared on modified substrates. The RMS roughness of the film was 2.87 nm on $1 \times 1 \ \mu m^2$ area. It should be noted that the other ionic liquid films had the similar morphologies and roughness although the figures are not shown here.

Table 1 lists the contact angles of distilled water on these films. Firstly, the contact angles of water on hydroxylated and aminated Si were below $5°$ and $59°$, respectively, which indicated that the hydrophilicity of hydroxylated surface was stronger than that of aminated surface. Secondly, the contact angle of water on each ionic liquid film on hydroxyl-terminated surface was almost equal with that on amino-terminated Si but not equal to that on bare hydroxylated or aminated substrates, inferring that ionic liquid films were successfully coated on pretreated Si substrates. Finally, the contact angles of water on IL106B and IL106A were further lower than it on IL106P.

The relationship between contact angle and surface energy is given by following equation:[21]

$$\gamma_L(1 + \cos\theta_{SL}) = 2\left[(\gamma_S^d \gamma_L^d)^{\frac{1}{2}} + (\gamma_S^p \gamma_L^p)^{\frac{1}{2}} + (\gamma_S^h \gamma_L^h)^{\frac{1}{2}}\right]$$

Here γ_L is the surface energy of the liquid and θ_{SL} is the contact angle of liquid on surface. The superscripts d, p, and h indicate the dispersion, polar, and hydrogen-bonding forces, respectively. The $\gamma_L, \gamma_L^d, \gamma_L^p$ and γ_L^h are constant for known liquid (i.e., for water $\gamma_L = 72.8$ mN/m, $\gamma_L^d = 29.1$ mN/m, $\gamma_L^p = 1.3$ mN/m, and $\gamma_L^h = 42.4$ mN/m). The surface energy of sample (γ_s) is the sum of γ_S^d, γ_S^p, and γ_S^h values.

So it is suggested that the larger the contact angle is, the lower the surface energy is.

Adhesion of ionic liquid films

Figure 5 shows the adhesion of substrates and ionic liquid films determined on contact mode AFM. It can be seen that adhesion of hydroxyl-terminated Si is much higher than that of amino-terminated Si, and when coated with IL106B or IL106A the adhesion of ionic liquid films increased with different degree on either hydroxylated or aminated Si. When coated with IL106P, the adhesion decreased greatly on hydroxylated and slightly on amino-terminated surfaces, respectively.

The reasons of above phenomena were mainly related to the surface energy. High surface energy results in strong interaction between surface and AFM tip. When the hydroxylated Si turned into aminated Si by orderly assembling APS on it, its surface energy decreased greatly, which could be proved by the difference
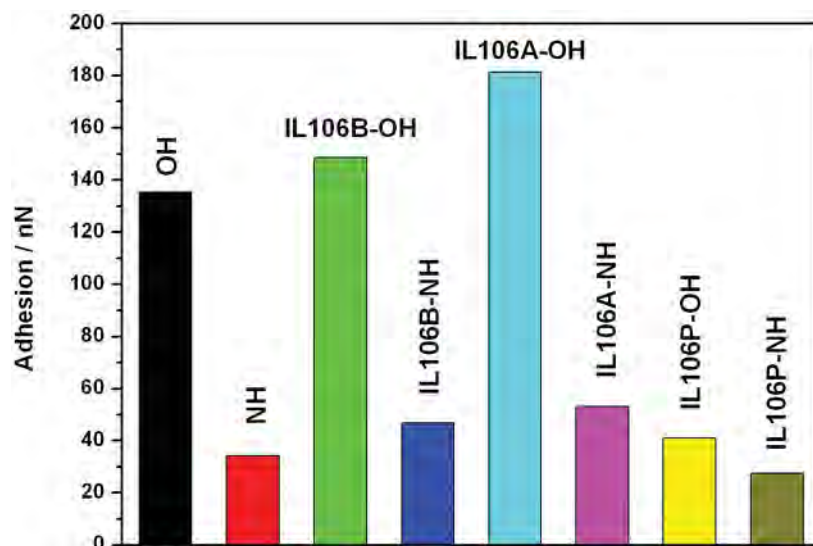

Figure 4. Morphology of ionic liquid film observed on tapping-mode AFM. This figure is available in colour online at www.interscience.wiley.com/journal/sia.

Figure 5. Adhesion of substrates and ionic liquid films. This figure is available in colour online at www.interscience.wiley.com/journal/sia.

between the contact angles of water on hydroxylated and aminated Si. So the adhesion of aminated Si was much lower than that of hydroxylated Si. In the presence of a thin liquid film, there exists meniscus/viscous effect between substrate and AFM tip.[22] So although the surface energy of IL106B and IL106A films was slightly lower than that of bare hydroxylated Si, their adhesion was higher than that of the latter. Furthermore, the surface energy of IL106P was much lower than that of hydroxylated Si and nearly equaled to that of amino-terminated Si, so its adhesion on hydroxyl-terminated Si was much lower than that of bare hydroxylated Si while its adhesion on amino-terminated Si was slightly lower than that of aminated Si.

Microtribological property of ionic liquid films

Figure 6 exhibits the friction coefficient of substrates and ionic liquid films in microscale. From these curves, it can be clearly seen that all friction coefficients decreased with the increase of testing load. Corresponding with their higher adhesion, bare hydroxylated Si, IL106B, and IL106A films coating on hydroxyl-terminated Si exhibited higher friction coefficient than other surfaces under testing load. Among three kinds of surfaces mentioned above, the hydroxylated Si had the highest friction coefficient. However, aminated surface, also without the protection of ionic liquids, performed low friction coefficient under low load. It was probably due to the presence of ordered APS assembled on it and the long chain of APS could decrease friction force by some degree. While the APS became disordered and less efficient under high load (about 13 and 16 nN), so the friction coefficient of aminated Si was nearly fixed and finally became higher than that of ionic liquid films on amino-terminated Si. The IL106P films on hydroxyl-terminated and amino-terminated Si showed lower friction coefficient than other ionic liquid films, which is corresponding to their lower adhesion. Nevertheless, for IL106P film, it owned lower adhesion while exhibited higher friction coefficient on amino-terminated Si than on hydroxyl-terminated Si. The main reason was presumed that the ordered long chain of APS interfered with ionic liquid moving.

Macrotribological property of ionic liquid films

Without the protection of ionic liquid films, the bare substrates of hydroxyl-terminated and amino-terminated Si were easy to be broken (lifetime <10 s) even at a mild test condition (0.1 N, 1 Hz), and the final friction coefficient is steady at 0.7.

Table 2 lists the friction coefficients and lifetimes of all kinds of ionic liquid films tested on UMT-2MT. Those of IL106A film on hydroxyl-terminated Si were not listed in here, because the film showed much poor wear resistance (lifetime <20 s) even at a mild test condition (0.1 N, 1 Hz).

Table 2. Friction coefficient and lifetime of modified Si surface coated with IL106B

Load/N	Friction Coefficient			Lifetime/s		
	1 Hz	2 Hz	4 Hz	1 Hz	2 Hz	4 Hz
(a) IL106B on hydroxyl-terminated Si						
0.1	0.12	0.13	0.14	>3600	>3600	>3600
0.2	0.11	0.13	0.13	>3600	>3600	>3600
0.4	0.11	0.12	0.12	>3600	~2100	~400
(b) IL106B on amino-terminated Si						
0.1	0.10	0.22	a	>3600	~100	<20
0.2	0.11	a	a	>3600	<20	<20
0.4	0.12	a	a	~3100	<20	<20
(c) IL106A on amino-terminated Si						
0.1	0.14	0.15	0.15	>3600	>3600	>3600
0.2	0.09	0.11	a	>3600	~600	<20
0.4	0.09	0.11	a	~1600	~300	<20
(d) IL106P on hydroxyl-terminated Si						
0.1	0.11	0.11	0.18	>3600	>3600	>3600
0.2	0.10	0.11	0.13	>3600	>3600	~730
0.4	0.11	0.12	0.11	>3600	~1300	~70
(e) IL106P on amino-terminated Si						
0.1	0.10	0.12	0.14	>3600	>3600	>3600
0.2	0.10	0.12	a	>3600	~420	<20
0.4	0.10	a	a	>3600	<20	<20

a Increased sharply to a large value at the beginning of test.
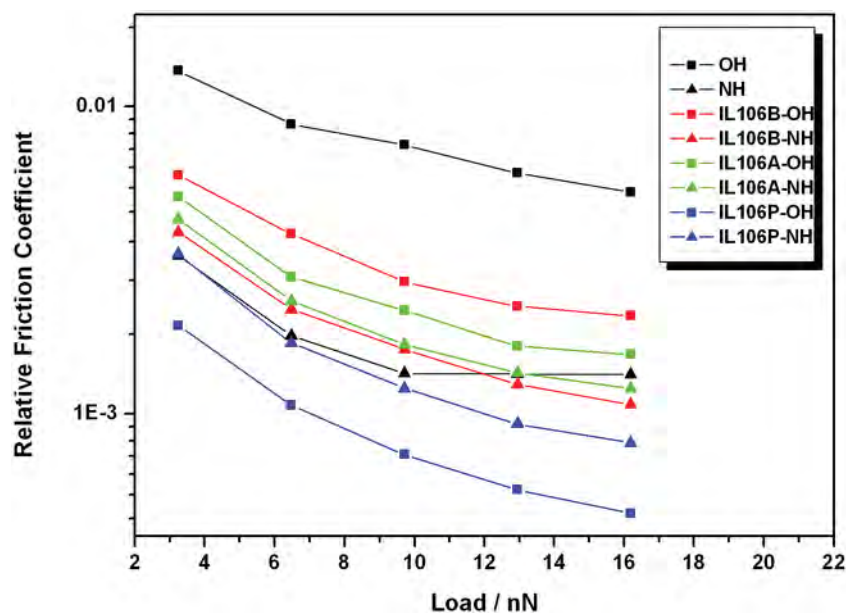
Figure 6. Friction coefficient of substrates and ionic liquid films. This figure is available in colour online at www.interscience.wiley.com/journal/sia.

It can be seen that the tribological properties of IL106B on hydroxyl-terminated Si (Table 2a) was better than that on amino-terminated Si (Table 2b). On the whole, the friction coefficient of IL106B on hydroxyl-terminated Si slightly increased with increasing frequency and decreased with increasing load. In contraries, IL106B film on amino-terminated Si performed good tribological properties only under low testing frequency (1 Hz). When testing frequency increases, the lifetime of IL106B film on amino-terminated decreased sharply and the film almost broke at the beginning of test.

The IL106A film on amino-terminated Si (Table 2c) presented high friction coefficient and long lifetime at a load of 0.1 N, and with the increase of testing load both the friction coefficient and the lifetime decreased. Only at a load of 0.2 N and frequency of 1 Hz, the IL106A film on amino-terminated Si had low friction (0.09) and long lifetime (>3600 s) simultaneously. Under higher load (0.2 and 0.4 N), the lifetime of the film decreased rapidly with testing frequency increasing.

The tribological properties of IL106P films on hydroxyl-terminated Si (Table 2d) were a little better than that on amino-terminated Si (Table 2e). On hydroxyl-terminated Si, the friction coefficient of IL106P film was almost fixed with the increase of load or frequency except that on a frequency of 4 Hz the friction coefficient decreased with the increase of load and its lifetime rapidly shortened at the same time. It could be clearly seen that under low load (0.1 N) the friction coefficient of IL106P film on amino-terminated Si slightly increased as testing frequency increasing and its lifetime is changeless (>3600 s). When testing frequency was fixed at 1 Hz, its friction coefficient and lifetime remained at 0.10 and >3600 s, respectively, with testing load increasing. While under other testing conditions, the wearability of the film became weak and the lifetime of the film reduced sharply.

From above results, it can be seen that there are great difference in the tribological properties between lubricated and unlubricated substrates. In microscale, the tribological properties of hydroxylated Si were greatly improved by the ionic liquid films. The main reason was that bare single-crystal silicon, as a kind of brittle material, would be penetrated by the tip owing to either brittle deformation or formation of cracks without the protection of mobile ionic liquids, and the ploughing of the tip into the substrates would result in catastrophic failure.[23,24] While the aminated Si were less affected, which mainly due to the presence of ordered APS assembled on it and the long chain of APS could decrease friction force by some degree. As to macrotribological properties, without ionic liquids films protection, the bare hydroxylated and aminated Si were easy to be broken (lifetime <10 s) even at a mild test condition (0.1 N, 1 Hz), which is owing to plastic deformation and phase transformation on the substrates. If normal load is beyond a critical value, material removal will occur and some of the surface materials will be torn away.[23,24] When protected with ionic liquids films, the tribological properties increased greatly in different degree.

By comparing the tribological properties of different ionic liquid films in details, it can be seen that IL106B and IL106P films were better than IL106A film. Although the IL106A film on amino-terminated owned the lowest friction coefficient (0.09) of all, its wearability under severe testing condition was poorer than IL106B and IL106P films. It is probably due to the inorganic anions of IL106B and IL106P, which are more stable than the organic anion of IL106A and difficult to decompose during tribo-test. Furthermore, the IL106B and IL106P showed the same tendency that their tribological properties on hydroxyl-terminated Si were slightly better than those on amino-terminated Si. The main reason is assumed that the ordered APS on amino-terminated Si decreased the mobility of IL106B and IL106P. While the IL106A film had better tribological properties on amino-terminated Si than on hydroxyl-terminated Si, which could be considered that the strong interaction between hydroxyl and carboxyl in adipate of IL106A resulted in the poor mobility of IL106A on hydroxyl-terminated Si.

Contrasting the results of the tribological properties of various surfaces in microscale and macroscale, it can be found that there are many differences between microtribology and macrotribology. Firstly, in microscale, the IL106P films have the best tribological properties, and much better than the other two ionic liquid films, while in macroscale, the 106P and 106B have comparable tribological properties and were better than 106A films. Secondly,

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on the whole, in microscale, the tribological properties of ionic liquid films on amino-terminated surface is better than that on hydroxyl-terminated surface, while in macroscale, situations were just the opposite except the IL106A films.

The reason of these large differences in tribological properties between microscale and macroscale is mostly due to their different tribological mechanism. In microscale tribology, the surface energy may play the major role that it affected the interaction between AFM tip and surfaces and then influenced the adhesion and the friction coefficient. However, in macroscale, as we proved in previous work,[16] the major factor that affected the tribological properties is the mobility of ionic liquids on substrate. When there is strong interaction between substrate and ionic liquid or factor, which interferes with ionic liquid moving, ionic liquid film would exhibit poor tribological properties.

Conclusions

Altogether, three kinds of ionic liquid films with thickness of about 4 nm were successfully prepared. The surface energy of these films was evaluated through testing their contact angle. Their microtribological properties were examined, and their macrotribological properties were also tested as comparison. The following conclusions are drawn:

(1) In microscale, 1-hexyl-3-methyl-imidazolium hexafluorophosphate (IL106P), which owned the lowest surface energy, possessed the lowest adhesion and friction coefficient, and bare aminated Si which had lower surface energy performed lower adhesion and friction coefficient than bare hydroxylated Si.

(2) In macroscale, 1-hexyl-3-methyl-imidazolium tetrafluoroborate (IL106B) and IL106P exhibited better tribological properties than 1-hexyl-3-methyl-imidazolium adipate (IL106A) due to their stable inorganic anions.

(3) The difference between microtribology and macrotribology is mostly caused by their different tribological mechanisms. In microscale, it is surface energy that greatly affects tribological properties, while in macroscale, the mobility of ionic liquid on substrate becomes the major factor.

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