Tribology International 42 (2009) 828–835

Contents lists available at ScienceDirect

Tribology International

journal homepage: www.elsevier.com/locate/triboint

Effect of cation on micro/nano-tribological properties of ultra-thin ionic liquid films

Wenjie Zhao [a,b], Yufei Mo [a,b], Jibin Pu [a,b], Mingwu Bai [a,*]

[a] State Key Laboratory of Solid Lubrication, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, China
[b] Graduate School of Chinese Academy of Sciences, Beijing 100039, China

ARTICLE INFO

Article history:
Received 24 January 2008
Received in revised form
28 October 2008
Accepted 31 October 2008
Available online 6 December 2008

Keywords:
Micro/nano-friction
Adhesion
Ionic liquids
Ultra-thin film
AFM

ABSTRACT

Room temperature ionic liquids (RTILs) have some unique characteristics which meet the requirements as high performance lubricants. In this work, three kinds of RTILs films with the same anion but different cations were prepared on single-crystal silicon wafer by dip-coating method. Thermal stability of the RTILs was evaluated using thermal gravity analysis in a nitrogen atmosphere. The morphology, nano-friction and nano-adhesion properties of the RTILs films were experimentally investigated at nano-scale using AFM/FFM. Chemical compositions of the films were characterized with a multi-functional X-ray photoelectron spectrometer. Micro-tribological properties of RTILs films were investigated using AISI-52100 steel ball in ball-on-plate configuration, and compared with perfluoropolyether. The worn surface morphologies were measured with a 3D optical surface profilometer. Results show that 3-butyl-1-methyl-imidazolium tetrafluoroborate exhibited the best anti-wear ability in comparison with the other three lubricants. RTILs films could be used as a kind of novel lubricant for application in M/NEMS. The corresponding friction-reduction and anti-wear mechanisms of the tested ultra-thin RTILs films under tested condition were proposed based on the experimental observation. The investigation revealed that friction-reduction and anti-wear properties of RTILs were strongly dependent on their chemical structures. For the friction at nano-scale, the flexibility and surface energy of the lubricant played significant role, while for the friction at micro-scale, both the rigid cycle structure and flexible chain of the RTILs played crucial role.

1. Introduction

Micro/nano-electromechanical systems (M/NEMS) have been increasingly demanded in many areas such as nano-technology, high density storage, optical communication, and biomedicine. Therefore, M/NEMS related research is being given greater attention. The surfaces in M/ NEMS are generally separated by a couple of nano-meters [1,2]. Accordingly, adhesion, stiction and friction are the major reasons that cause the failure of M/NEMS [2,3].

Perfluoropolyethers (PFPEs) have many intrinsic properties such as very low vapor pressure, good chemical and thermal stability, low surface tension and high contact angle. Hence PFPEs have been widely applied in nuclear, precision instrument, and aerospace industries as lubricating oils. They have been also commonly used as lubricating films in M/NEMS and magnetic disk drive industry to reduce the friction and wear of the interface [4–6]. However, PFPEs are catalytically degraded by strong nucleophilic agents and strong electropositive metals, which together with the high cost of PFPEs, limit their application in some fields [7–9]. Therefore, the development of new alternatives to PFPEs is a continuous effort.

Room temperature ionic liquids (RTILs) have received much attention due to their unique chemical and physical properties, such as negligible vapor pressures, non-flammability, high thermal stability, low melting point, broad liquid range, a highly solvating capacity, for both polar and non-polar compounds. Thus they are expected to be good candidates to replace PFPEs as versatile lubricants for different sliding pairs. Ye found that RTILs can be used as a novel versatile lubricant and exhibited excellent friction reduction, anti-wear performance and high load-carrying capacity [10], Liu and co-workers reported some tribological properties of RTILs [11–13].

The previous research on RTILs as a lubricant focused on evaluation of various types of RTILs, and also on synthesizing novel functionalized RTILs [14,15]. However, so far little has been reported on the tribological properties of RTILs applied as ultra-thin film (about 2 nm) on a polished silicon or DLC surface, which is also critical to their application in M/NEMS [16]. The purpose of this research was to examine the tribological

* Corresponding author. Tel.: +86 931 4968080; fax: +86 931 8277088.
E-mail address: mwbai@LZB.ac.cn (M. Bai).

0301-679X/$ - see front matter © 2008 Elsevier Ltd. All rights reserved.
doi:10.1016/j.triboint.2008.10.020

properties of ultra-thin film made from three kinds of RTILs with different cations. The effect of cations on the tribological properties of RTILs with the same anion was investigated.

2. Experimental

2.1. Materials

P-doped single side polished single-crystal silicon (1 0 0) wafers (obtained from GRINM Semiconductor Materials Co. Ltd., Beijing) with a surface roughness of about 0.2 nm and a thickness of 0.5 mm were used as the substrate. Three kinds of RTILs including 3-butyl-1-methyl-imidazolium tetrafluoroborate, tetraalkylphosphonium tetrafluoroborate and N-butyl-pyridinium tetrafluoroborate, marked as L-B104, I-P and I-N, respectively, were synthesized using the similar procedures as proposed in previous references [17–20]. All other reagents were of analytical grade and used as received. The chemical structures of the RTILs we used are given in Fig. 1. For comparison, PFPE (formula $HOCH_2CF_2O–(CF_2–CF_2O)_m–(CF_2O)_n–CF_2CH_2OH$, m and n are integers, MW = 3800, commercial name Zdol-3800, was purchased from Aldrich Chemical Company and used as received).

2.2. Pretreatment of silicon wafers

All glass vials used were cleaned by thoroughly rinsing with deionized (DI) water and acetone and then dried at 100 °C in an oven. Cleaned silicon wafers were immersed in a freshly prepared Piranha solution (7:3 (v/v) mixtures of 98% H_2SO_4 and 30% H_2O_2) at 90 °C for 40 min to produce hydroxyl groups on the surfaces [21]. Then the substrates were extensively rinsed with DI water and blown dry with a stream of nitrogen.

2.3. Film preparation

The solution of RTILs was firstly prepared in acetone with a suitable concentration. The solution concentration of Zdol-3800, L-B104, I-P and I-N was 0.15% (w/v), 0.06% (w/v), 0.1% (w/v), and 0.1% (w/v), respectively. Then the silicon wafer was slowly dipped into and withdrawn from a tank containing the solution with a uniform velocity 60 μm/s, and then it was immersed in the solution for up to 120 s in order to obtain a uniform coating. Si wafer was allowed to dry in air in clean room prior to the following measurements.

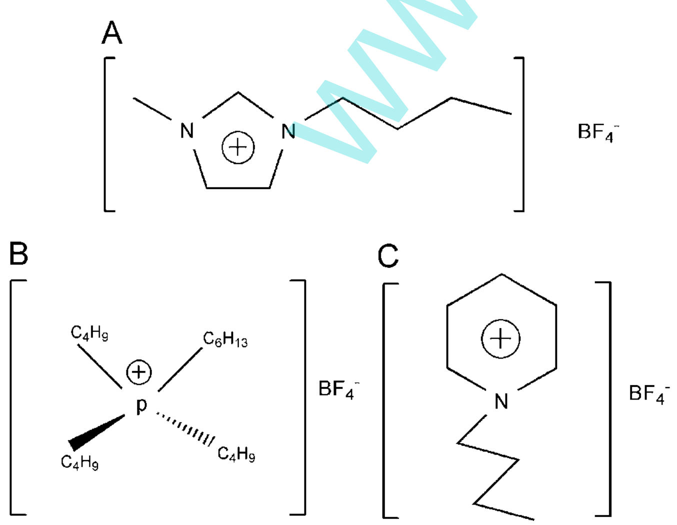

Fig. 1. Molecular structures of the ionic liquids: (A) 3-butyl-1-methyl-imidazoliuml tetrafluoroborate, (B) tetraalkylphosphonium tetrafluoroborate and (C) N-butyl-pyridinium tetrafluoroborate.

2.4. Characterization of films

The film thickness was measured on an L116-C ellipsometer (Gaertner, USA) equipped with a He–Ne laser ($\lambda = 632.8$ nm) at a fixed incidence angle of 50°. The thickness was recorded at an accuracy of ± 0.3 nm on ten locations on each sample.

In order to identify the wetting property of the specimen surface, the static contact angle of water on the film surface was determined on a CA-A contact angle meter (Kyowa Science Company Ltd., Japan). Five replicate measurements were conducted at different regions of the film surface and the measurement error was below 2°. The averaged contact angles were given in this article.

A PHI-5702 multi-functional X-ray photoelectron spectrometer (XPS), was applied for the determination of the chemical compositions and structures of the surfaces coated with RTILs. As parameters, a pass energy of 29.35 eV, Mg-Kα ($h = 1253.6$ eV) radiation for excitation and a take off angle of 36° were used. Chamber pressure was about 3×10^{-8} Torr. The binding energy of contaminating carbon of C_{1s} at 284.8 eV was used as the reference.

2.5. Measurement of micro/nano-tribological characteristics

The micro-friction and wear properties of all these films were evaluated using a commercial ball-on-plate tester. An AISI-52100 steel ball of 3.18 mm diameter was fixed in a stationary holder sustained by a beam and the samples were then mounted on a reciprocating table. The ball moved horizontally with respect to the sample surface with a frequency of 1 Hz (10 mm/s, unless otherwise noted) and a traveling distance of 5 mm. The change in friction coefficient was monitored versus sliding times or cycles. The initiation of wear on the sample surface led to increase in friction coefficient, and a sharp increase of friction coefficient indicated the failure of film. All the tests were conducted at room temperature and a relative humidity of 30–40%.

Atomic force/friction microscopes (AFM/FFM) are widely used in nano-tribology and nano-mechanics studies. In this paper, nano-tribological behaviors of RTILs films were characterized with an AFM/FFM controlled by CSPM4000 electronics, using the contact mode. The measurement of frictional forces was accomplished by monitoring the lateral torsion of the cantilever as a function of the applied load. The detailed procedure has been

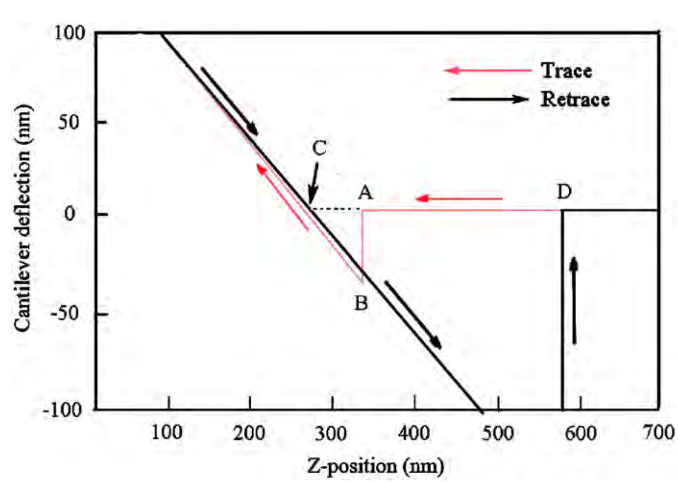

Fig. 2. A typical force–distance plot and schematic illustration for adhesion force calculation.

described in previous publications [22,23]. Commercially available triangular Si_3N_4 cantilever (CSC21/Si_3N_4/Al BS, overall Si_3N_4 coating, backside Al-coated) with an announced spring constant of 2 N/m and a coated tip with a curvature radius of about 10 nm

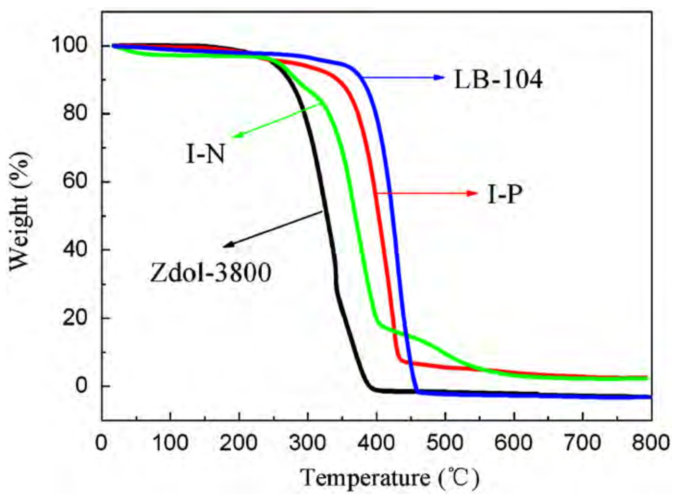

Fig. 3. TGA curves of Zdol-3800 and three kinds of ionic liquids.

Table 1
Static contact angles of various films..

Sample	Contact angle (deg)
SiO_2/Si	<5
I-P	30 ± 2
I-N	25 ± 2
L-B104	21 ± 2
Zdol-3800	100 ± 2

was employed. No attempt was made to calibrate the torsional force constant, the output voltages were directly used as the relative frictional force. For the comparison to be valid, the same cantilever/tip was used during the experiment unless specified otherwise. Furthermore, to avoid the influence of molecules which may transfer to the tip on the AFM/FFM experiment, the tip was scanned on a cleaved mica surface to remove these physically adsorbed molecules. Each value shown represents an average over at least 10 different measurements. All the experiments were performed at a relative humidity level of 20–30% at room temperature.

2.6. Adhesion measurements

AFM has been used extensively to measure adhesive forces between surfaces at nano-scale. The adhesive force between the AFM tip and the film surfaces under ambient condition is shown in Fig. 2. The adhesive force (pull-off force) was calculated by multiplying the cantilever spring constant by the horizontal distance between points C and D [4,24].

3. Results

3.1. Thermal behaviors of Zdol-3800 and RTILs

Thermal stability of lubricants was examined by thermogravimetric analysis (TGA) between 20 and 800 °C at a calefactive rate of 10 °C /min. As shown in Fig. 3, all RTILs showed little weight loss below 300 °C which corresponds to an extremely low vapor pressure and hence meets the demand of high performance lubricant. All RTILs showed better performance than Zdol-3800 in terms of thermal stability. At the chosen test conditions, L-B104 was the most stable RTILs, its thermal degradation started at 400 °C and completed at 450 °C.

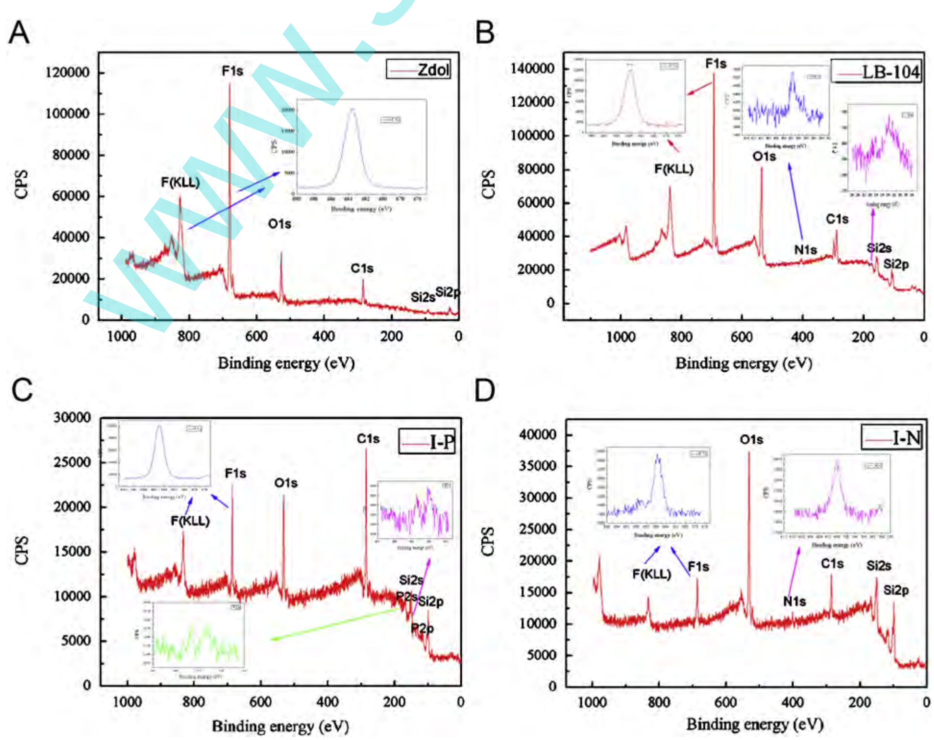

Fig. 4. XPS spectra of: (A) Zdol-3800, (B) L-B104, (C) I-P and (D) I-N.

3.2. Measurement of contact angle and thickness of films

Contact angle measurement is an effective way to reflect the variation of solid surface chemical composition. Table 1 lists the ultra-pure water contact angles on hydroxylated silicon surface and various surfaces coated with lubricant. The hydroxylated silicon surface is hydrophilic, with the water contact angle below 5°. When the RTILs and Zdol-3800 chemically adsorbed onto the silicon surface, the contact angle increased to 30°, 25°, 21°, 100°, respectively, which indicates that films were coated on the silicon. In order to compare the tribological properties of different lubricants, the thickness of all the films we made in this article is about 2 nm.

3.3. Composition and morphology

In order to confirm presence of the surface modifying agents (RTILs) on the surface and to verify the practicability of the surface modification procedure, XPS measurements were performed. Fig. 4 depicts the XPS scan survey spectra of both Zdol-3800 and three kinds of RTILs surface. Every one of the scan survey spectra shows four elements: fluorine (F_{1s}), carbon (C_{1s}), oxygen (O_{1s}) and silicon (Si_{1s}, Si_{2p}). It indicates that Zdol-3800 and RTILs were coated successfully on the silicon surface. From the XPS spectra of the elements on the silicon surface lubricated with RTILs, it is found that the peaks of B1s which appeared in all three kinds of RTILs, while P2p appeared only in I-P, which indicates that, the lubricants were coated successfully on the silicon surface. Because B and F are concomitant, anion cannot live solely without cation, if we can find F in the spectra, we can speculate that BF_4^- is existent in the film, and so is the cation. In a word, Zdol-3800 and RTILs films are coated successfully on the silicon surface.

Fig. 5 shows 2D surface morphology of Zdol-3800 and three kinds of RTILs. From Fig. 5A–D, the micro-roughness in root-mean-square (RMS) of the films were estimated to be less than 0.4 nm over an area of 1 μm × 1 μm, these observations indicates that the lubricant molecules spreaded evenly on the silicon surface.

3.4. Adhesive force measurements under ambient conditions

The adhesive force of Zdol-3800 and three kinds of RTILs films measured by AFM are summarized in Fig. 6. As shown in Fig. 6, Zdol-3800 showed the smallest adhesive force. The adhesive force

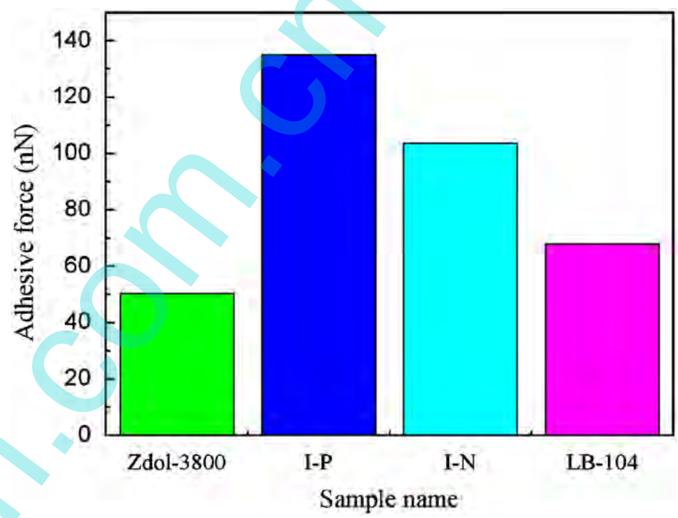

Fig. 6. Adhesion force curves of Zdol-3800, L-B104, I-P and I-N films measured in ambient air.

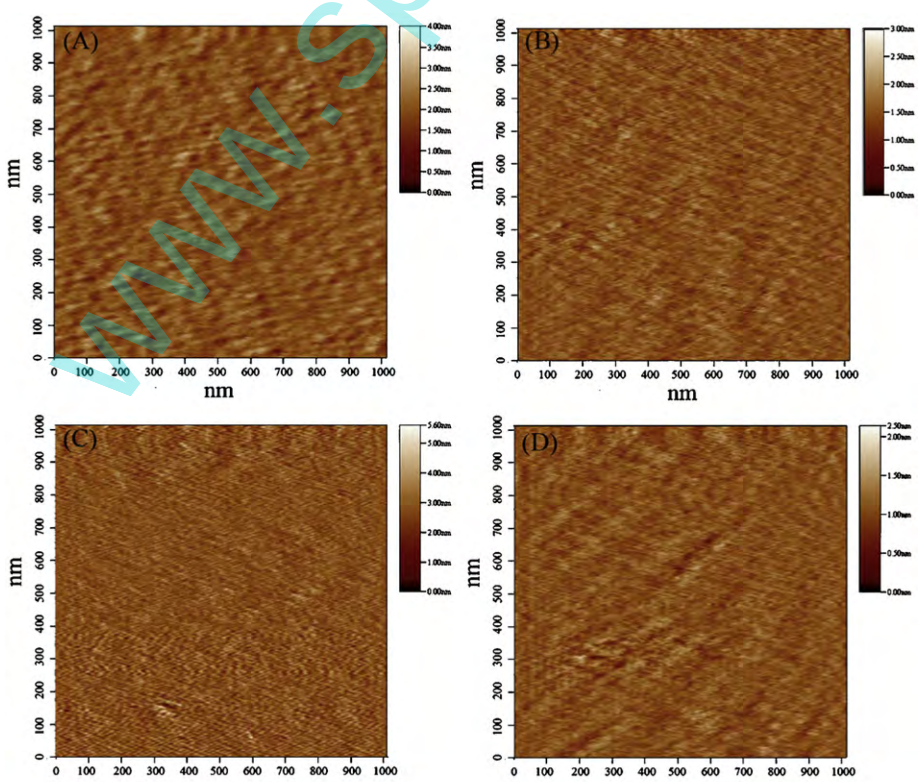

Fig. 5. Two-dimensional AFM images of: (A) Zdol-3800, (B) L-B104, (C) I-P and (D) I-N.

of L-B104 is between Zdol-3800 and I-N. I-P showed the biggest adhesive force. The adhesive force was related to the chemical structure and elements of the film. Further discussion will be gone in Section 4.2.

3.5. Nano/micro-tribological properties

3.5.1. Nano-tribological properties

To investigate the nano-friction properties of Zdol-3800 and three kinds of RTILs films, the friction force versus normal load curves were measured in a friction measurement under increasing normal loads. As seen from Fig. 7, L-B104 and I-N exhibited higher friction in comparison with Zdol-3800. The friction was different at small loads, but with increasing load the difference of I-P and I-N decreased. I-P contains many soft branched chains, which showed small friction. Compared to the above three kinds of RTILs films, Zdol-3800 exhibited lowest friction. Further discussion will be gone in Section 4.3.

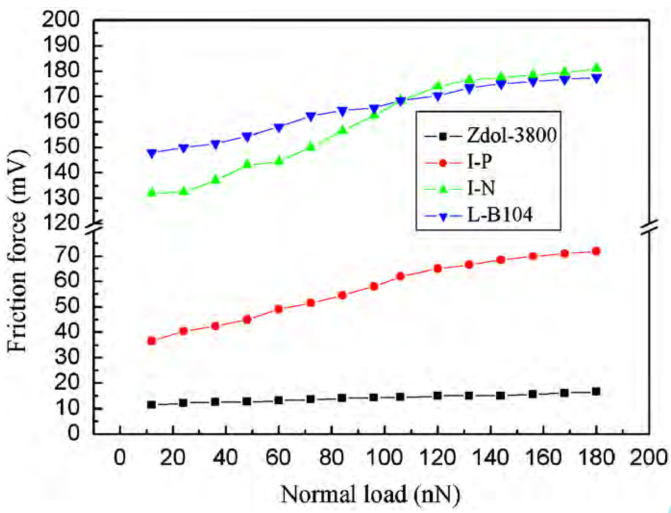

Fig. 7. Friction force versus normal load curves for Zdol-3800, L-B104, I-P and I-N films at a frequency of 1 Hz.

3.5.2. Micro-tribological properties

Fig. 8 shows the friction coefficients and anti-wear durability of Zdol-3800 and three kinds of RTILs films as functions of sliding cycles against steel ball.

For Zdol-3800 film, as shown in Fig. 8A, the friction coefficient was about 0.15 at the normal load of 60 mN. When the normal load rose to 100 mN, the friction coefficient decreased to about 0.1 and remained stable at sliding cycles below 1200 cycles. When sliding cycles exceeded 1250 cycles, the friction coefficient increased sharply to 0.6, which indicated that the friction-reduction effect played by Zdol-3800 film diminished under the test condition. When the normal load rose to 150 mN, sliding cycles reaching 200, the friction coefficient sharply increased to 0.7, so the durability was 200 cycles.

As shown in Fig. 8B, L-B104 recorded a friction coefficient of about 0.13, which kept almost constant with increasing sliding cycles at a load of 100 mN. When the normal load rose to 200 mN, the friction coefficient slightly decreased to 0.07, which was still almost stable under all sliding cycles, but the friction coefficient abruptly increased at a sliding load of 400 mN, 50 sliding cycles, this indicates that wear of the L-B104 film occurred and the film failed.

Fig. 8C shows the variation of friction coefficients and anti-wear durability of I-P film on Si substrates against steel ball with sliding cycles. It can be seen that I-P film recorded friction coefficient about 0.19 under a slight load of 60 mN, and the

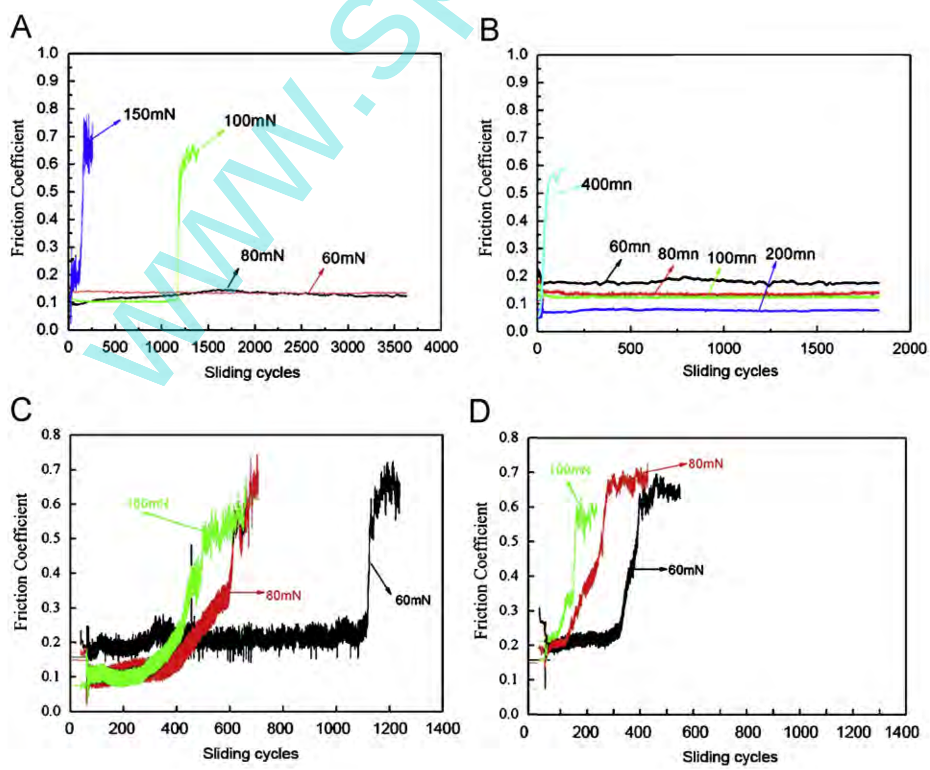

Fig. 8. Friction coefficients as function of sliding cycles for: (A) Zdol-3800, (B) L-B104, (C) I-P and (D) I-N sliding against AISI-52100 steel ball at normal load between 60 and 400 mN and a sliding velocity of 1 Hz.

registered anti-wear durability is about 1150 cycles in this case. With increasing normal load, anti-wear durability of the I-P film decreased dramatically, and it failed instantly at a load of 100 mN with just 500 sliding cycles. Fig. 8D shows the variation of friction coefficients and anti-wear durability of I-N film. It indicates that I-N film recorded friction coefficients about 0.15 under a slight load of 60 mN, and the registered anti-wear durability is 400 cycles in this case. With the increase of normal load, anti-wear durability of I-N film decreased dramatically, and it failed instantly at a load of 100 mN with only 150 sliding cycles.

From above results, it can be concluded that L-B104 was much superior to other three kinds of films in the test range of the loads in terms of wear resistance and load-carrying capacity in sliding against steel ball counterpart. Compared to the L-B104 film on the Si surface, it is evident that I-P and I-N films showed poorer tribological properties, especially under relatively larger loads.

3.6. 3D surface morphology of the worn surfaces

3D morphologies of the worn surfaces were exhibited as shown in Fig. 9, from the pictures we can see that different lubricants show different tribological performance at the same test condition, which is a load of 80 mN, a sliding time of 700 s, and a sliding frequency of 1 Hz. The results are in agreement with micro-friction test. From L-B104, Zdol-3800, I-P to I-N, the depth of worn surface increased greatly, so L-B104 showed the best tribological performance and I-N showed the worst tribological performance.

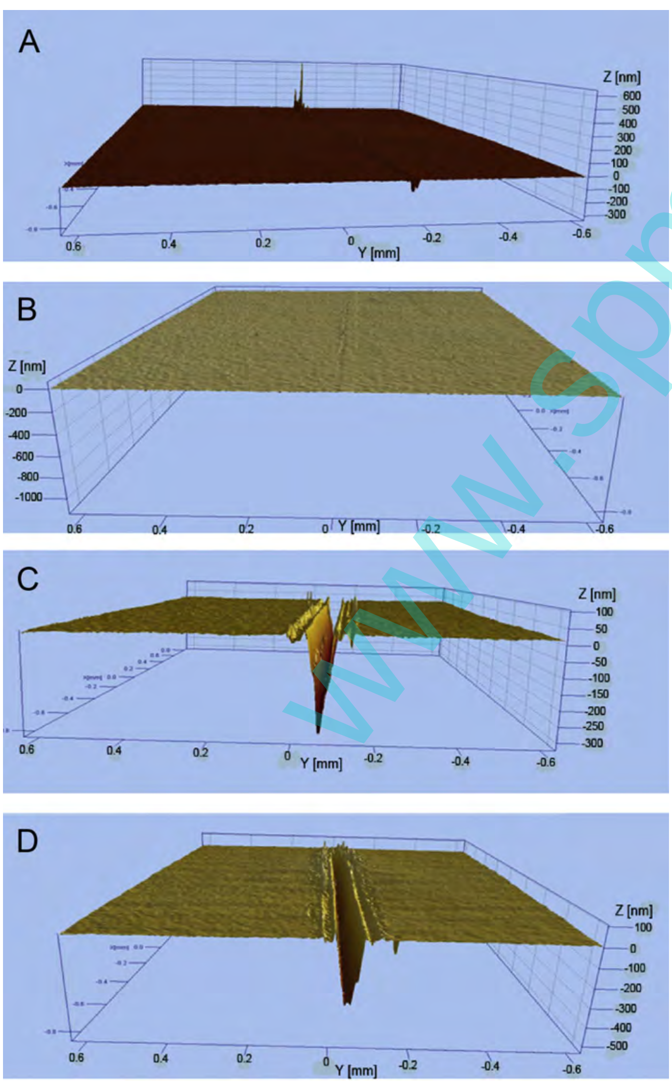

Fig. 9. Three-dimensional morphology of the worn surfaces at the same test condition (a load of 80 mN, a sliding time of 700 s and a sliding frequency of 1 Hz). From above to below, they are: (A) Zdol-3800, (B) L-B104, (C) I-P and (D) I-N, respectively.

4. Discussion

4.1. Film formation

It is considered that in the course of film formation, ionic liquid is similar with self-assembly film. Alkyltrichlorosilane [CH_3–$(CH_2)n$-$SiCl_3$, ATS] SAM, for example, was formed due to the reactivity of silyl chloride moiety with hydroxyl groups on the semiconductor silicon. In other words, the head-group provided chemisorption to the substrate [25–27]. So it is suggested that parts of the RTILs was immobilized on the silicon surface by reaction of the anion with the surface hydroxyl groups as represented in Fig. 10 (taking LB-104 as an example) [28,29]. Such an immobilized layer coupled with an added layer of a mobile species is suitable for providing satisfactory lubrication performance in the M/NEMS devices.

4.2. Adhesion mechanism

It is well known that, when the lubricant films were disordered and hydrophilic, they would easily form meniscus by themselves or the adsorbed water molecules, thus they had higher adhesive force, however, when the lubricant films were hydrophobic and ordered, they would show low adhesion [3,30]. Zdol-3800 contained fluorine element, the film was hydrophobic and its surface energy was lower than other three kinds of RTILs films, it tended to form densely packed, highly ordered film, so it showed the biggest contact angle and the smallest adhesive force. L-B104 and I-N had similar rigid cycle structure and branch chains, so their contact angle and adhesive force did not show much difference. Compared with the above three lubricant films, I-P had many branched chains and would not form densely packed, highly ordered film, the small water droplet may easily penetrate through the film and form meniscus, so it showed the biggest adhesive force.

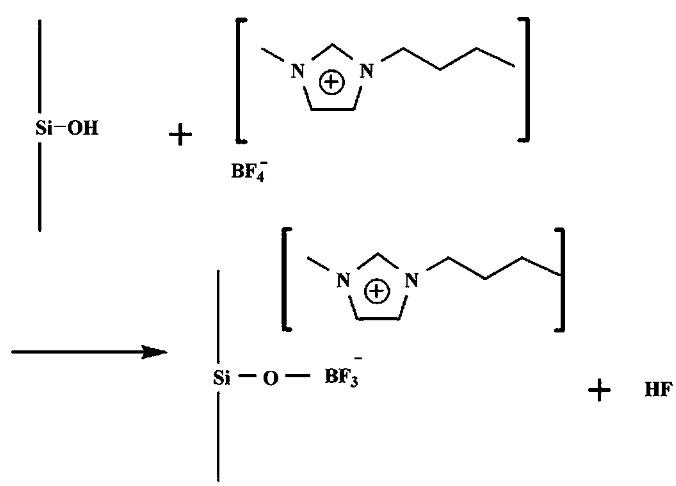

Fig. 10. Schematic diagram illustrating reactions leading to the deposition of film on Si substrates.

4.3. Nano-friction mechanism

The difference in nano-friction is attributed to three potential factors: firstly, intra-molecular energetic barriers to rotation of the rigid cycle structure; secondly long-range inter-molecular steric interactions within the plane of the bulkier groups [31,32]; and finally surface energy [33,34]. If the surface energy is much bigger, it is easily to form meniscus by themselves or the adsorbed water molecules, they had higher adhesive force due to the capillary force and hydrogen bond, which would led to larger shearing strength and larger friction. As seen from the Fig. 6, L-B104 and I-N contained rigid cycle structure and their flexibility was poor, they need much energy to overcome intra-molecular energetic barriers to rotation of the rigid cycle structure, so they exhibited larger friction. The friction was different at small loads because of their difference in branched chains. With increasing load, their difference decreased in the testing range. I-P contained many soft branched chains, its flexibility was better, so the friction was small. Compared to the above three kinds of RTILs films, Zdol-3800 had free linear chains so it could bound strongly to the silicon, it tended to form densely packed, highly ordered film, which had good flexibility, so the friction was the least. From the results obtained from experiments, it is also found that friction is in the same order with the surface energy and adhesive force. So it is suggested that the tribological properties of lubricants are determined by the flexibility and surface energy of lubricant for the friction at nano-scale.

4.4. Micro-friction mechanism

Lubricant was used to reduce friction and resist wear during the sliding. Compared to the friction at nano-scale, the loads employed were much larger for the friction at micro-scale. In this case, the tribological properties may be not only determined by the soft chains but also by the rigid cycle structure. The soft chains which were flexible can be used to decrease the friction and the rigid cycle structure was used to resist the wear during the test. L-B104 contained both rigid cycle structure and flexible chains, so it showed the best tribological properties among the lubricants used in this study. Zdol-3800 bonded strongly to the silicon and also had free linear chains, so it showed better tribological properties. I-P had many branched chains but without rigid cycle structure, I-N had rigid cycle structure but lack of flexible chain, so both of them showed large friction.

5. Summary and Conclusions

In summary, Zdol-3800 and three kinds of RTILs films were prepared and characterized successfully. The adhesion, micro/nano-tribological properties of these films were investigated, while Zdol-3800 was used for comparison. Their adhesive force consisted with the ultra-pure water contact angle and nano-friction. LB-104 films on hydroxyl-terminated surface showed excellent friction-reduction and anti-wear properties. The friction-reduction and anti-wear mechanism of the RTILs were dependent on their chemical structures. From the results obtained from the experiment, it is concluded that the tribological properties were close related to the flexibility and surface energy of lubricant film for the friction at nano-scale, however, at micro-scale friction, tribological properties may be determined not only by the flexibility of lubricant but also by rigid cycle structure. LB-104 nano-film has potential application in M/NEMS which needs better durability.

Acknowledgments

We are grateful for the financial support of the National Natural Science Foundation of China (NSFC 50675217), National 973 Program (2007CB607601), and Innovative Group Foundation (50421502).

References

[1] Gui J. Tribology challenges for head-disk interface toward 1 Tb/in^2. IEEE Trans Magn 2003;39:719–21.
[2] Hsu SM. Nano-lubrication, concept and design. Tribol Int 2004;7:537–45.
[3] Bhushan B, Kasai T, Kulik G, Barbieri L, Hoffmann P. AFM study of perfluoroalkylsilane and alkylsilane self-assembled monolayers for anti-stiction in MEMS/NEMS. Ultramicroscopy 2005;105:176–88.
[4] Liu HW, Bhushan B. Nanotribological characterization of molecularly thick lubricant films for applications to MEMS/NEMS by AFM. Ultramicroscopy 2003;97:321–40.
[5] Sinha SK, Kawaguchi M, Kato T, Kennedy FE. Wear durability studies of ultra-thin perfluoropolyether lubricant on magnetic hard disks. Tribol Int 2003; 36:217–25.
[6] Kato T, Kawaguchi M, Sajjad MM, Choi J. Friction and durability characteristics of ultrathin perfluoropolyether lubricant film composed of bonded and mobile molecular layers on diamond-like carbon surfaces. Wear 2004;257: 909–15.
[7] Caporiccio G, Flabbi L, Marchionniand G, Viola GT. The properties and applications of perfluoropolyether lubricants. J Synth Lubr 1989;6:133–49.
[8] Mori S, Morales W. Tribological reactions of perfluoroalkylpolyether oils with stainless steel under ultrahigh vacuum conditions at room temperature. Wear 1989;132:111–21.
[9] Mivake S, Wang M, Ninomiya S. Nanotribological properties of perfluoropolyether-coated magnetic disk evaluated by vertical and lateral vibration wear tests. Surf Coat Technol 2006;200:6137–54.
[10] Ye CF, Liu WM, Chen YX, Yu LG. Room-temperature ionic liquids: a novel versatile lubricant. Chem Commun 2001;1:2244–5.
[11] Xia YQ, Wang SJ, Zhou F, Wang HZ, Lin YM, Xu T. Tribological properties of plasma nitrided stainless steel against SAE52100 steel under ionic liquid lubrication condition. Tribol Int 2006;39:635–40.
[12] Liu XQ, Zhou F, Liang YM, Liu WM. Tribological performance of phosphonium based ionic liquids for an aluminum-on-steel system and opinions on lubrication mechanism. Wear 2006;261:1174–9.
[13] Wang HZ, Lu QM, Ye CF, Liu WM, Cui ZJ. Friction and wear behaviors of ionic liquid of alkylimidazolium hexafluorophosphates as lubricants for steel/steel contact. Wear 2004;256:44–8.
[14] Mu ZG, Liu WM, Zhang SX, Zhou F. Functional room-temperature ionic liquids as lubricant for an aluminum-on-steel system. Chem Lett 2004;33: 524–5.
[15] Mu ZG, Zhou F, Zhang SX, Liang YM, Liu WM. Effect of the functional groups in ionic liquids molecules on the friction and wear behavior of aluminum alloy in lubricated aluminum-on-steel contact. Tribol Int 2005;38:725–31.
[16] Yu B, Zhou F, Mu ZG, Liang YM, Liu WM. Tribological properties of ultra-thin ionic liquid films on single-crystal silicon wafers with functionalized surfaces. Tribol Int 2006;39:879–87.
[17] Holbery JD, Seddon KR. The phase of 1-alkyl-3-methylimidazolium tetrafluoroborates: ionic liquids and ionic liquid crystals. J Chem Soc Dalton Trans 1999:2133–9.
[18] Bradaric CJ, Downard A, Kennedy C, Robertson AJ, Zhou Y. Industrial preparation of phosphonium of ionic liquids. Green Chem 2003;5:143–52.
[19] Fuller J, Carlin RT, Osteryoung RA. The room temperature ionic liquid 1-ethyl-3-methylimidazolium tetrafluoroborate: electrochemical couples and physical properties. J Electrochem Soc 1997;144:3881–5.
[20] Ding SF, Wei W, Zhao GC. Direct electrochemical response of cytochrome c on a room temperature ionic liquid, N-butylpyridinium tetrafluoroborate, modified electrode. Electrochem Commun 2007;9:2202–6.
[21] Schreiber F. Structure and growth of self-assembling monolayers. Prog Surf Sci 2000;65:151–257.
[22] Shon Y-S, Lee Jr S, Colorado R, Perry SS, Lee TR. Spiroalkanedithiol-based SAMs reveal unique insight into the wettabilities and frictional properties of organic thin films. J Am Chem Soc 2000;122:7556–63.
[23] Lee S, Shon Jr Y-S, Colorado R, Guenard RL, Lee TR, Perry SS. The Influence of packing densities and surface order on the frictional properties of alkanethiol self-assembled monolayers (SAMs) on gold: a comparison of SAMs derived from normal and spiroalkanedithiols. Langmuir 2000;16:2220–4.
[24] Yang S, Zhang H, Hsu SM. Correction of random surface roughness on colloidal probes in measuring adhesion. Langmuir 2007;23:1195–202.
[25] Bunker BC, Carpick RW, Assink RA, Thomas ML, Hankins MG, Voigt JA, et al. The impact of solution agglomeration on the deposition of self-assembled monolayers. Langmuir 2000;16:7742–51.
[26] Wang YL, Lieberman M. Growth of ultra-smooth octadecyltrichlorosilane self-assembled monolayers on SiO_2. Langmuir 2003;19:1159–67.
[27] Wang MJ, Liechti KM, Wang Q, White JM. Self-Assembly silane monolayers: fabrication with nanoscale uniformity. Langmuir 2005;21:1848–57.

[28] Nainaparampil JJ, Phillips BS, Eapan KC, Zabinski JS. Micro-nano behavior of DMBI-PF_6 ionic liquid nanocrystals: large and small-scale interfaces. Nanotechnology 2005;16:2474–81.
[29] Valkenberg MH, DeCastro C, Hölderich WF. Immobilisation of ionic liquids on solid supports. Green Chem 2002;4:88–93.
[30] Bhushan B. Handbook of micro/nano-tribology. 2nd ed. Boca Raton, FL: CRC Press; 1999.
[31] Kim HI, Graupe M, Oloba O, Koini T, Imaduddin S, Lee TR, et al. Molecularly specific studies of the frictional properties of monolayer films: a systemic comparison of CF_3^-, $(CH_3)_2CH^-$ and CH_3^- terminated films. Langmuir 1999;15:3179–85.
[32] Kim HI, Koini T, Lee TR. Systematic studies of the frictional properties of fluorinated monolayers with atomic force microscopy, comparison of CF_3- and CH_3-terminated films. Langmuir 1997;13:7192–6.
[33] Beake BD, Leggett GJ. Friction and adhesion of mixed self-assembled monolayers studied by chemical force microscopy. Phys Chem Chem Phys 1999;1:3345–50.
[34] Ren SL, Yang SR, Zhao YP. Micro and macro tribological study on a self-assembled dual-layer film. Langmuir 2003;19:2763–7.