Nano/Micro-Tribological Properties of Ultrathin Functionalized Imidazolium Ionic Liquid Films on Silicon Wafer

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Extended Abstract

Ionic liquids (ILs) are considered as a new kind of lubricant for micro/nanoelectromechanical system (M/NEMS) due to their excellent thermal and electrical conductivity. However, so far, only few reports have investigated the tribological behavior of molecular thin films of various ILs. Evaluating the nanoscale tribological performance of ILs when applied as a few nanometers-thick films on a substrate is a critical step for their application in MEMS/NEMS devices. To this end, four kinds of ionic liquid carrying methyl, hydroxyl, nitrile, and carboxyl group were synthesized and these molecular thin films were prepared on single crystal silicon wafer by dip-coating method. Film thickness was determined by ellipsometric method. The chemical composition and morphology were characterized by the means of multi-technique X-ray photoelectron spectrometric analysis, and atomic force microscopic (AFM) analysis, respectively. The nano and micro tribological properties of the ionic liquid films were investigated. The morphologies of wear tracks of IL films were examined using a 3D non-contact interferometric microscope. The influence of temperature on friction and adhesion behavior at nano scale, and the effect of sliding frequency and load on friction coefficient, load bearing capacity and anti-wear durability at micro scale were studied. Corresponding tribological mechanisms of IL films were investigated by AFM and ball-on-plane micro-tribotester. Friction reduction, adhesion resistance and durability of IL films were dependent on their cation chemical structures, wettability and ambient environment.

Keywords: Ionic liquid; Lubricant; Thin film; Friction; Wear

1. INTRODUCTION

Ionic liquids are considered as potential lubricants. Their strong electrostatic bonding compared to covalently bonded fluids, leads to very desirable lubrication properties. They also prossess desirable properties such as negligible volatility, nonflammability, high thermal stability or high decomposition temperature, efficient heat transfer properties, low melting points, as well as compatibility with lubricant additives [1]. Unlike conventional lubricants that are electrically insulating, ionic liquids can minimize the contact resistance between sliding surfaces because they are conducting, and conducting lubricants are need for various electrical applications [2]. In addition, ILs have high thermal conductivity which helps to dissipate heat during sliding. The use of ionic liquids instead of hydrocarbon base oil has potential to dramatically reduce air emissions.

In this study, AFM-based adhesion, friction measurements are presented for silicon substrate coated with the ionic liquids of interest. A friction force microscopy (FFM) was employed to investigate the interfacial structure and tribological properties of thin IL films. A glass sphere probe was used instead of normal silicon nitride probes to reduce the contact pressures produced by sharper silicon nitride tips. Conventional ball-on-flat data is used in conjunction with AFM experiments in order to compare friction and wear properties at micro and nano scale.

2. EXPERIMENTAL

Silicon wafers (100 P-doped) were treated in fleshly prepared Piranha solution (volume ratio 7:3 of 98% H_2SO_4 and 30% H_2O_2) at 90 °C for 30 min to get a hydroxyl-terminated surface. The ionic liquids used in this study are 1-propyl-3-methylimidazolium chloride, 1-ethanol-3-methylimidazolium chloride, 1-propionitrilel-3-methylimidazolium chloride and 1-propionic acid-3-methylimidazolium chloride abbreviated as MIMCH-CL, MIMOH-CL, MIMCN-CL and MIMCOOH-CL, respectively. The lubricants were applied on single crystal silicon using dip-coating technique and then dried at 90 °C for 10 min. The thicknesses of the films after dip-coating were measured by the ellipsometric method.

Adhesion and friction force measurements were carried out using a commercial CSPM 4000 AFM/FFM microscopy in ambient conditions (20 °C, 15%RH). A colloidal probe was prepared by gluing glass sphere with a radius of 37.5 μm onto a tipless cantilever (normal force constant 2 N/m). The colloidal probe was cleaned by ethanol and acetone in turn before use. For all experiments the same cantilever was used in this comparative study. Furthermore, to avoid influence of molecules which may transfer to tip on the FFM experiments, the colloidal probe was scanned on cleaved mica surface to remove physical adsorb molecules.

Friction coefficient and durability at microscale were evaluated using a pin-on plate tribometer in reciprocating mode. A Si_3N_4 ball moved horizontally with respect to the sample surface with sliding frequency between 1 to 4Hz and applied normal load between 60 and 400 mN. The friction coefficient and sliding times were recorded automatically by computer. All measurements were conducted at room temperature and a relative humidity of 15 %.

3. RESULTS AND DISCUSSION

3.1 NANOTRIBOLOGICAL BEHAVIOR

Si substrate data are provided for comparison. Strong adhesive force was observed on the hydroxylated Si surface at humidity of 15%, on which the adhesive force was about 184 nN. After the ILs were coated, the adhesive forces were decreased to 121, 152, 136 and 138 nN, respectively. The adhesive force has been observed to decrease in the following order: MIMOH-CL > MIMCOOH-CL > MIMCN-CL > MIMCH-CL. The hydrophilic property of cationic end groups in IL films facilitated the formation of a meniscus, which increases the tip-sample adhesion. The adhesive force is lowest in MIMCH-CL since it has greatest amount of relative hydrophobic end groups among the four IL samples.

Base on the FFM experimental data, the MIMCH-CL and MIMCN-CL exhibited lowest friction. The results imply that the hydrophilic property of cationic end group samples facilitated sliding on the spherical tip on the surface. However, values of friction for MIMCOOH-CL and MIMOH-CL are higher than the data for MIMCH-CL and MIMCN-CL. Due to

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water and lubricant molecules are more likely to form a meniscus as the spherical tip approaches the surface. This provides greater resistance to tip sliding and leading to higher values of friction.

3.2 MICROTRIBOLOGICAL BEHAVIOR

Tribological performance was evaluated for hydroxylated Si substrate and ionic liquid coated surfaces with film thickness of about 2 nm. Without the protection of ionic liquid films, the coefficient of hydroxylated Si substrate increased sharply and was stable to a constant value of about 0.65.

In order to compare friction and wear properties, conventional ball-on-plat tribometer experiments were conducted on the same samples. Fig. 1a-d contain plots of the coefficient of friction as a function of the number of sliding cycles at normal loads range from 60 to 400 mN. As shown in Fig. 1a, the friction coefficients of MIMCH-CL were 0.12 and 0.09 at normal loads of 60 and 100 mN, respectively. When the normal load rose to 200mN, the friction coefficient rose sharply over 0.6 before reaching 450 cycles, implying that the lubricant film failed. The friction coefficients of MIMOH-CL were averaged at 0.14, 0.10, 0.11 and 0.06 at normal loads of 60, 100, 200 and 300mN, respectively. As shown in Fig. 1b, the MIMOH film was failed at normal load of 400 mN. As shown in Fig.1c and d, the friction coefficient of MIMCN-CL and MIMCOOH-CL were averaged at 0.13 and 0.11 at all loads. Only a small rise in the coefficient of friction was observed for both MIMOH-CL and MIMCOOH-CL surface, indicating low surface wear. However, both MIMOH-CL and MIMCOOH-CL samples exhibited gradually change in value of friction coefficient. This is attributed to the transfer of lubricant molecules to the Si_3N_4 ball and the interaction of the transferred molecules with the lubricant still attached on the Si surface, which will increase the friction force.

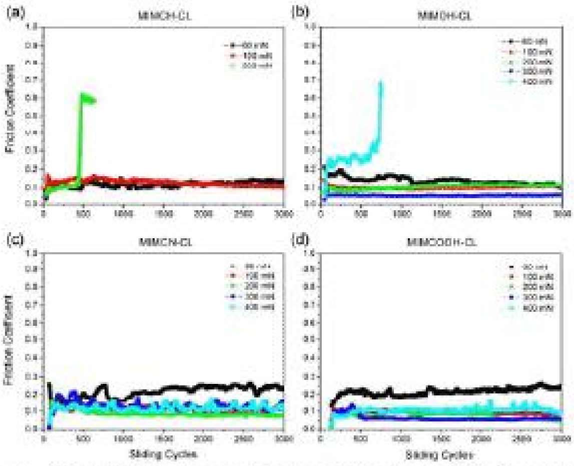

Fig. 1 Plot of friction coefficients as function of sliding cycles for MIMCH-CL (a), MIMOH-CL (b), MIMCN-CL (c) and MIMCOOH-CL (d) film on silicon

Fig. 2a-d showed the effect of sliding frequencies on coefficient of friction for all IL film at normal load of 60 mN. As shown in Fig. 2a, the friction coefficient of MIMCH-CL was averaged about 0.15 at relative mild condition (below 2 Hz). When the sliding frequency rose to 3 Hz, its friction coefficient sharply increased over 0.6 in several minutes, which indicated that the IL films failed completely under higher frequency reciprocating movement. At the same time, the MIMOH-CL, MIMCN-CL and MIMCOOH still maintained low friction coefficient of 0.13, 0.11 and 0.14 under high frequency of 4 Hz, as shown in Fig. 2b-d. According this result, it is seen that the MIMOH-CL, MIMCN-CL and MIMCOOH exhibit longer anti-wear durability under high frequency reciprocating slide, compared with the MIMCH-CL.

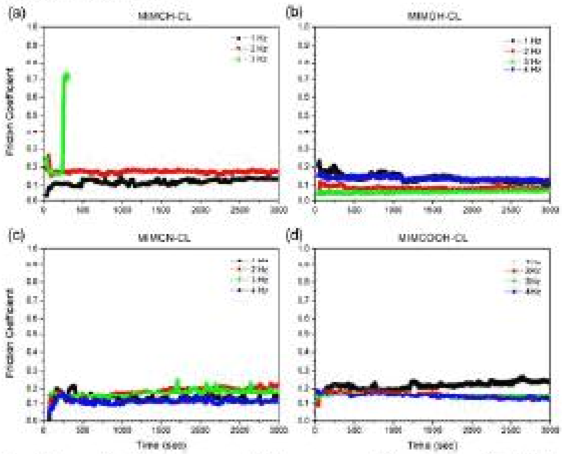

Fig.2 Plot of friction coefficients as function of sliding frequency for MIMCH-CL (a), MIMOH-CL (b), MIMCN-CL (c) and MIMCOOH-CL (d) films at a normal load of 60 mN

4. CONCLUSIONS

This study has demonstrated that four kinds of ionic liquid films with thickness ranging from approximate 2 to 60 nm were prepared as uniform coatings by dip-coating method. Adhesion and friction experiments at nanoscale were carried out using a colloidal probe. Base on topography adhesion and friction data, all IL films are prone to attach to the silicon substrate surface, leading to more uniform coatings and lowered adhesion and friction. The MIMCN-CL and MIMCH-CL show favorable lubrication, as seen from the adhesion and friction being less than that of MIMOH-CL, MIMCOOH-CL and uncoated silicon in all cases. The microscale friction and wear of the four ionic liquid films were evaluated at load range of 60-400 mN and the sliding frequency range of 1-4 Hz. All ionic liquids show favorable friction reduction and durability. MIMCN-CL and MIMCOOH-CL exhibited low friction coefficient and long durability even at a normal load of 400 mN. The MIMOH-CL, MIMCN-CL and MIMCOOH-CL exhibited lower friction and better anti-wear durability at high frequency sliding (4 Hz) compared with MIMCH-CL in micro scale. Thus, from a tribological point of view, the ionic liquids show strong potential as lubricant for MEMS because they have desirable thermal and tribological properties.

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