Ionic liquid self-assembled monolayer and ion exchange for surface force control

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Adhesion and lateral force were controlled by the formation of a self-assembled monolayer combined with the surface ion exchange of ionic liquids on a silicon surface. In this study, the functionalized imidazolium ionic liquids were designed and synthesized with the aim of controlling surface force. N-[3-(Trimethoxysilyl)propyl] ethylenediamine molecules were first self-assembled onto a surface as an anchor layer and then 1-propionic acid-3-methylimidazolium chloride were successfully grafted onto the amino-modified surface. The surface force was changed by surface ion exchange in various anionic solutions. The self-assembly and ion exchange processes were detected by means of attenuated total reflectance-Fourier transform infrared spectrometry and further confirmed by X-ray photoelectron spectra. Adhesion and friction behaviors were systematically investigated by atomic force/friction force microscope. The results indicated that anions played a great role in determining surface properties. Furthermore, surface adhesion and friction can be possibly quantitatively determined by the counter- anions on the surface. Copyright © 2011 John Wiley & Sons, Ltd.

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Introduction

Adhesion control of surfaces has been widely used in many important applications including microfluids, microfabrication, drug delivery, gene sensor, and biomimetic materials. Surface textures and chemical modification are commonly used in magnetic data storage systems and microelectromechanical systems (MEMS) to reduce surface force to lessen the possibility of mechanical failure.\textsuperscript{[1,2]} A number of fabrication methods were used to generate micro/nano hierarchical structures for surface force control, including laser interface patterning,\textsuperscript{[3]} plasma/chemical etching,\textsuperscript{[4]} soft photolithography,\textsuperscript{[5]} sol-gel processing and solvation casting,\textsuperscript{[6]} self-assembled monolayers,\textsuperscript{[7,8]} electrical deposition,\textsuperscript{[9]} dip-pen printing,\textsuperscript{[10]} and atomic force microscopy (AFM) local anodic oxidation,\textsuperscript{[11–15]} etc. Among the surface modification methods, the formation of self-assembled monolayers (SAMs) proved to be a simple and economic technique for the adhesion control of solid surfaces. Several reports have demonstrated that the adhesive properties of SAMs are closely related to their intrinsic chemical composition and structures including chain length and terminal group.\textsuperscript{[16–21]} SAMs with longer chains are generally more densely packed than the shorter ones. On the other hand, altering the terminal groups from apolar to polar results in an increase of surface energy. In addition, introducing a functional group such as diacetylene, peptide, and sulfone into straight hydrocarbon chains to construct robust SAMs is another way to control their packing densities and surface energies.

Ionic liquids (ILs) are low-melting-point salts that represent a new class of ionic media. They are composed of ion pairs containing bulky, asymmetric cations and anions. The low melting points of ILs compared with classic molten salts are due to the particular chemical structures of their anions and cations. ILs possess a combination of unique characteristics including negligible volatility, nonflammability, high thermal stability, and conductivity, which have motivated research and led to various applications such as organic synthesis, catalysis, photochemistry, and so on. On the other hand, as is well known to tribologists, these characteristics are also just what high-performance lubricants demand. Very harsh friction conditions require lubricating oils to have high thermal stability and chemical inertness. The decomposition temperatures of imidazolium ILs are generally above 350°C, some are even as high as 480°C, and together with the low temperature fluidity means that ILs can function in a wide temperature range. In addition, low volatility makes ILs applicable under vacuum, especially for spacecraft application. The above-mentioned properties of ionic liquids also make them excellent lubricants.\textsuperscript{[22,23]}

Different with large scale mechanical system, MEMS cannot be lubricated with lubrication oils, but use an ultrathin lubrication film whose thickness is well below a few tens of nanometers. The viscous force comes largely from the viscosity of lubricant films and the meniscus force, rather than the applied loads; this dictates the extent of friction and the mechanisms of lubrication failure. The perfluoropolyethers of nanometer thickness are the most widely used lubricants in miniaturized devices, but usually experience metal catalytic degradation and are normally expensive. The potential of ILs in thin film lubrication was exploited by a number of researchers aiming to replace perfluoropolyethers.\textsuperscript{[24–29]} The molecular structure, the counter anion, the length of substituted alkyl chains, and the functional groups, have key effects on the adhesion and tribological behavior of IL films. The interaction between lubricant and surface cannot only determine the wetting of the lubricant but also determine its durability.\textsuperscript{[30–32]}

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The anions have a more complicated effect on surface force in that they cannot only change the viscosity but also interfacial energy. In previous researches on ionic effect,[33,34] the IL molecules were directly dip-coated on the surface, and the anions were usually embedded in the films. Therefore, the results may have been easily affected by the cations. In this study, the IL molecules were self-assembled onto the surface, and then the anions were replaced to the outmost layer by an ion exchange method to minimize avoiding the impact of other ions.

Experimental

Materials

N-[3-(Trimethoxysilyl)propyl]ethylenediamine (TSA) was purchased from Aldrich Chemical Co., St. Louis, MO. 1-Propionic acid-3-methylimidazolium chloride ([PAMI]Cl) were synthesized and purified according to reported procedures.[35] Acetone, isopropanol, and ethanol were all analytical reagents. NaBr, NaNO3, NaClO3, LiNSO3CF3,2 were obtained from Aldrich Chemical Co. and Shanghai Chemical Co., Shanghai, China. All reagents were used as received.

Substrate preparation

The P (100) polished single crystal silicon wafer used as the substrate was obtained from Grinm Semiconductor Materials Co., Beijing. Silicon wafers were cleaned and hydroxylized in piranha solution (mixture of 7:3 v/v 98% H2SO4 and 30% H2O2) at 90°C for 30 min. After that, wafers were ultrasonically rinsed with deionized (DI) water.

Preparation of self-assembled monolayer

Aliquots of 20 μL of TSA were dissolved in 20 mL of a mixture of acetone and DI water (5:1 v/v). Hydroxylated substrates were immersed in fresh TSA solutions for 24 h. After that, the modified Si substrates were rinsed with isopropanol, ethanol, and acetone in turn to remove the other physisorbed ions and molecules. The TSA-modified silicon substrates were dipped into a 0.02% (w/v) dilute solution of [PAMI]Cl in ethanol for 2 min and withdrawn from the solution at a velocity of 60 μm/s. To accelerate the acid-amide reaction between [PAMI]Cl and TSA, these films were heated from room temperature at a rate of 60°C/min, stabilized at 180°C for 10 min in nitrogen and then cooled in a desiccator. A monolayer of [PAMI]Cl was produced on top of the TSA film because the terminal amino groups in TSA can react with the carboxyl groups in [PAMI]Cl to form chemical bonds.

Characterization

A FAT32 contact angle goniometer was used to measure the static water contact angle of the films. At least three points were measured for each specimen, and measurement error was ±1. The ellipsometer thickness measurements were performed on an XLS-100 spectroscopic ellipsometer (Woolum, J.A. Woolum Co., Lincoln, NE), which was equipped with a He–Ne laser set at an incident angle of 50°. A real refractive index of 1.46 was set for the organic layers. The data were collected from ten different positions for each specimen to get the averages. The molecular composition and structure of the surface were examined with a PHI-5702 multitechnique X-ray photoelectron spectrometer (XPS, Physical Electronics Co., Chanhass, MN), using a pass energy of 29.35 eV, an excitation source of Mg-Kα radiation (hv = 1253.6 eV) and take-off angle of 36°. The chamber pressure was about 3 × 10⁻⁸ torr during testing. Peak deconvolution and quantification of elements were accomplished using the software and sensitivity factors supplied by the manufacturer. The binding energy of adventitious carbon (C1s: 284.8 eV) was used as a reference. Fourier transformation infrared (FTIR) spectra were recorded on a Bruker IFS 66/V FTIR spectrometer (Bruker Optics Inc., Ettlingen, Germany) with a Ge attenuated total reflectance accessory. The samples were placed in contact with the flat surface of a semispherical Ge crystal, which served as the optical element. The spectra were collected for 32 scans with a resolution of 4 cm⁻¹. The background was collected using the accessory with no sample placed on it. To eliminate the effect of H2O and CO2, the pressure in the sample chamber and optical chamber was kept below 6.0 × 10⁻⁴ MPa.

Nanotribological study

A nanotribological study of the films was performed using a CSPM 4000 AFM (Benyuan Co., Beijing, China) using contact mode. Commercially available rectangle Si3N4 cantilevers and the force constant of the cantilever was calculated at 1.8 N/m using the individually measured thickness, width, and length.[36] The above dimensions were determined by a scanning electron microscope. During adhesion measurement, the laser beam is focused on the back of the AFM cantilever to detect the cantilever’s deflection as it interacts with the surface beneath it. The reflected beam is directed onto a split photodiode detector, which produces a voltage signal proportional to the cantilever deflection. The sample beneath the cantilever is moved using a piezoelectric transducer. In the force measurements, motions in the x and y directions are disabled, the piezoelectric tube is used to move the surface in the z direction, and the cantilever deflection is continuously measured. The surface is first moved toward the cantilever until the tip contacts the surface and then is retracted from the cantilever until the tip snaps off from the surface. The adhesion force was obtained from measuring the deflection of the cantilever at the point where the tip pulls off from the surface after contact. In this research, at least 200 different measuring locations were carried out for each scan range, and also, at least ten consecutive adhesion force measurements in each location were taken and averaged. The friction force was calibrated by the method described in.[37] A series of measurements of the friction-load behavior was recorded from the friction loops. All force measurements were conducted at relative humidity of 20%. Repeated measurements were within 5% of the average value for each sample.

Results and discussion

The amino-terminated surface has found vast applications in many fields. Here, the TSA monolayer served as the anchor layer, and chemical bonds were formed between the amino layer and the incoming [PAMI]Cl molecules. Generally, the formation of the SAMs can be monitored by thickness and the static water contact angle measurement. It is assumed that one CH2 unit, considering NH2 or CO as CH2 n length, is 1.4 Å long in all-trans configuration chains.[38] Therefore, the complete TSA and [PAMI]Cl–TSA have theoretical thicknesses of about 11 and 21 Å,
respectively. Every 20 min, two parallel specimens of each kind were picked out of the solution, cleaned and blown dry for the thickness measurement. When the measured thickness reached the corresponding theoretical thickness, it was assumed that a complete monolayer was formed. If the reaction time were prolonged, the thickness would be more than the theoretical values, indicating that multilayers instead of monolayers formed because the formation of SAMs is very sensitive to preparation conditions such as solvent and temperature, and the depositing time to form a monolayer varies.[39,40] As shown in Table 1, the measured ellipsometer thickness of TSA and the [PAMI]Cl–TSA layer are 9.7 and 19.1 Å, respectively, which were very close to the theoretical molecule length. Before the organic layer formed on the silicon surface, the water contact angle was about 0°. After the formation of amino-terminated SAMs and IL SAMs, the contact angle rose to around 46° and 61°, respectively, which agree well with what has been reported.[26,41] The results indicate that the high quality TSA and [PAMI]Cl–TSA SAM have been deposited onto the substrate.

For the exchange of anions on the SAM surface, the SAM-modified silicon substrates were immersed in an aqueous 5 mM solution of NaBr, NaNNO3, NaClO4, LiNSO2CF3, respectively, and incubated at room temperature for 12 h. After that, the samples were rinsed extensively with DI water and dried with a steam of nitrogen. The formation process is illustrated in Fig. 2.

Moreover, the exchange process of anions on the silicon surface was confirmed by XPS. Figure 3 shows the XPS of the surface after ion exchange. The XPS survey spectra showed silicon (Si 1 s, 2p), chlorine (Cl 2p), carbon (C 1 s), nitrogen (N 1 s), oxygen (O 1 s), and fluoride (F 1 s). As shown in Fig. 3(a), peaks of Cl2p and F 1 s at 198.4 eV and 688.5 eV can be assigned to Cl atom in [PAMI]Cl film and F atom in [PAMI][SO2C6F3]2 film, respectively. In the N1s spectrum that is shown in Fig. 3(b), there are peaks of 398.6, 399.8, and 400.7 eV. While the peak at 398.6 eV is assigned to the N atom in the amine group, the peak that appears at 399.8 eV can be attributed to the N atom bonded to the carboxyl group (O = C–N*). The peak at 400.7 eV can be assigned to the H-bonded amino group.[42–44]

Friction force measurements were performed with a friction force microscope. A histogram of the adhesive force between the AFM tip and various film surfaces are shown in Fig. 4. Strong adhesion was observed on the silicon surface at a relative humidity of 20%, on which the adhesive force was 16.8 nN. After [PAMI]Cl ionic liquid molecules self-assemble onto surface, the adhesive force decreases to 12.9 nN. This indicates that the ionic liquid film exhibited a different adhesion with the silicon substrate, because the –OH group was covered by Cl– on the upper layer of the surface. There is a significant discrepancy in the adhesive force of the surface after ion exchange. Among them, NiSO2CF3 exhibited the lowest adhesive force, about 4.3 nN, while the adhesive forces of Br– and ClO4– appeared at 11.5 and 6.7 nN, respectively. The friction force measurements of various ionic surfaces were

<table>
<thead>
<tr>
<th>Samples</th>
<th>Thickness (Å)</th>
<th>Contact angle (°)</th>
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<tbody>
<tr>
<td>Hydroxylated Si</td>
<td>18.3</td>
<td>~ 0</td>
</tr>
<tr>
<td>TSA layer</td>
<td>9.7</td>
<td>46</td>
</tr>
<tr>
<td>[PAMI]Cl–TSA layer</td>
<td>19.1</td>
<td>61</td>
</tr>
</tbody>
</table>

The grafting of [PAMI]Cl molecules to TSA SAMs was further confirmed by means of the attenuated total reflectance-Fourier transform infrared (ATR-FTIR) spectra. In Fig. 1, it can be seen that the peak frequencies for asymmetric and symmetric methylene vibrations, Vas (CH2) and Vs (CH2) appear at 2922 and 2854 cm–1, respectively.
investigated by the method of linear applied load. Figure 5 presents the plots of friction force versus load curves for the surfaces of silicon substrate and [PAMI]Cl IL SAMs with various anions. As shown in the figure, all of the anions covering the surface showed a lower friction force than that of the silicon surface. Different friction forces appear at [PAMI]Cl IL SAMs bearing different counter-anions by ion exchange. The tendency of the friction force agrees well with the change in adhesion measurements, which correlates with the surface energy. The drop in friction force is a result of desorption of water molecules and the corresponding decrease of water menisci contribution. The results indicated that surface adhesion and friction can be possibly quantitatively determined by the counter-anions on the surface. It provides a novel and simple technique for anion detection.

Conclusions

In summary, adhesion and friction were controlled by the formation of various ionic surfaces combining IL SAMs with ion exchange. In this study, the IL molecules were self-assembled onto the surface, and then the anions were replaced to the outmost layer by an ion exchange method to minimize the impact of other ions. The self-assembly and ion exchange process were confirmed by a Ge ATR-FTIR and XPS. The effect of adhesive and friction forces on the surface bearing various anions was investigated systematically. The results indicated that anions played a great role in determining surface properties. Furthermore, surface adhesion and friction can be possibly quantitatively determined by the counter-anions on the surface. It provides a novel and simple technique for applications of anion detection microfluidics and MEMS anti-adhesion.

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References