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Investigation of the tribological behavior of 3-mercaptopropyl trimethoxysilane deposited on silicon

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Abstract

3-Mercapto-propyl trimethoxysilane (MPTS) thin film was prepared on hydroxylated silicon substrates by a self-assembling process and the terminal −SH group in the film was in situ oxidized to $-SO_3H$ group. Atomic force microscope (AFM) and X-ray photoelectron spectroscopy (XPS) were used to characterize the thin films. The tribological properties of the as-prepared thin films sliding against a steel ball were evaluated on a friction and wear tester. It was found that the macroscopic friction coefficients for coating times more than 1 h ranged between 0.1 and 0.2 whereas the value for short coating time was as high as 0.7. And the friction coefficient was higher for the SAM with functional group $-SO_3H$ compared to the SAM having −SH group. Surface energy of the substrate can be obviously increased when the terminal group (−SH) of self-assembly monolayers was oxidized into sulfonate one ($-SO_3H$) which can reduce the adhesion force of the moving surfaces. It was also found that the frictional behaviors of MPTS coated silicon surface sensitive to applied load and sliding velocity.

Keywords: MPTS; Self-assemble film; Characterization of the film; Friction and wear behavior

1. Introduction

Micro-electromechanical-systems (MEMS) technology has been receiving much attention in the past decade for its potential applications in areas such as communications, mechatronics and biomedicals [1,2]. However, currently many potential applications for MEMS are not really practical, as many studies have revealed the profound negative influence of stiction, friction and wear on the efficiency, power output, of microdevices [3]. Obviously, it is essential to supply super lubrication for MEMS for successful applications.

Self-assembled monolayers (SAMs) are ordered molecular assemblies formed by chemical adsorption of an active surfactant on a solid substrate surface [4,5]. SAMs can be spontaneously formed by immersion of an appropriate substrate into a solution of an active surfactant in an organic solvent. The molecularly thin feature, the relatively strong chemical bonded interface, and the simple preparation process make SAMs inherently manufacturable and thus technologically interesting for building efficient lubricants.

Some researchers use self-assembled monolayer (SAM) of MPTS to mediate the film deposition because it can be obtained expediently and has been previously used to make functional monolayers, and the thiol groups (−SH) can be oxidized into sulfonic acid groups ($-SO_3H$) easily [6,7]. A number of studies have been done on the tribological properties of different SAMs [8–10], but the study of the MPTS SAM on the tribological behavior is much lacking. The MPTS SAM films constructed by strong chemical bonds can be prepared by the self-assembly technique. Despite experimental as well as recent theoretical advances, a general understanding of MPTS SAM tribological investigation is still lacking. In this study, some work was done to research the preparation and tribological property of MPTS SAM on silicon substrates.

In the paper, MPTS SAM was prepared and the tribological properties were investigated. Many means, such as X-ray photoelectron spectroscopy (XPS), friction and wear tester, atomic force microscopy (AFM), etc. had been applied to characterize the structure and tribological properties of thin films in the paper. In this study we report on the fabrication, tribological behavior

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of MPTS SAM, specially the sensitivity of the frictional behavior with respect to variables such as coating time, applied load, and sliding velocity.

2. Experimental

2.1. Sample preparation

2.1.1. Materials

A single-crystal silicon wafer polished on one side was used as substrate for the SAM film transfer. MPTS were purchased from Sigma–Aldrich (Deisenhofen, Germany) and used as received. All other chemicals used in chemical manipulations were of reagent grade. Water was deionized water obtained from a Barnstead Nanopure apparatus.

2.2. Preparation of film

Silicon substrates were immersed for 30 min in Piranha solution (H_2SO_4:H_2O_2 = 7/3 v/v) at 90 °C to make hydroxy radicals on the surfaces. Then the substrates were carefully rinsed with deionised water and dried. After that the hydroxide substrates were dipped into the dehydrated benzene solution containing 0.5 mM of MPTS solution for 12 h. At last the substrates were cleaned ultrasonically with chloroform, acetone and deionised water in turn to remove the other physisorbed ions or molecules and dried for 1 h at 120 °C, then cooled in a desiccator. The oxidization of the −SH groups to the desired $-SO_3H$ groups was carried out by dipping the substrates into the solution of 30% nitric acid at 80 °C for 1 h, followed by washing with distilled water and dried in nitrogen.

2.3. Experimental apparatus and measurements

XPS is a highly diagnostic tool for the assessment of the chemical state of elements [11,12]. In this paper XPS analysis was conducted on a PHI-5702 XPS system, using Mg Kα radiation operating at 250 W and a pass energy of 29.35 eV. It is well known about the importance to investigate the film morphology in the research of the self-assembly technique. Atomic force microscopy (AFM) has been employed to study the morphology of RE films, because not only it has great vertical resolution but also it allows the measurement of other interesting parameters which can help us to find more value information about films, such as roughness, grain size and surface cross-section. The AFM topographic measurements and patterning of RE films were performed with a SPM-9500 unit (Shimadzu Corp., Japan). The interfacial property, particularly the wettability and the roughness of the solid surface, has very significant importance in the study of the preparation and the tribological properties of the thin films. The study of contact angles of the samples was on the OCA-20 measurement apparatus (DataPhysics Instruments GmbH). Contact angles have been measured on 10 locations on the all the samples. All results on each sample were averaged and the accuracy obtained by this method.

The tribological properties of coated silicon substrate with MPTS SAM sliding against a ball made of steel were evaluated on a Kyowa DF-PM model one-way reciprocating friction tester at ambient conditions (23 °C). The sliding velocity and stroke were 3 mm/s and 6 mm. The normal force was selected as 50 mN. The coefficient of friction and sliding passes were recorded automatically. The friction coefficient was an average of five test results. Prior to the friction and wear test, all the samples were cleaned in an ultrasonic bath with acetone for 10 min and then dried in hot air.

3. Results and discussion

3.1. Characterization of the film

Fig. 1 shows the AFM images of hydroxide silicon substrate, the MPTS SAM and oxidized MPTS SAM. Fig. 1(b)–(d) shows a series of AFM images of the MPTS SAM on silicon substrates, which were prepared from solution of MPTS with different immersion times ranging from 1 min to 24 h. From 15 to 30 min, with increasing immersion time the surface coverage increase and the surface morphology changed significantly. As can be seen, this increase is caused by an increasing number of MPTS islands. From 30 to 60 min, the density of the islands decreased as aggregation occurred, and the substrate surfaces became densely covered. After 24 h a flat surface with a R_a roughness of approximately 0.5 nm can be observed indicating that perfect monolayer coverage is reached after a prolonged period of deposition.

The mean roughness (R_a) were 0.20, 0.527 and 0.159 nm, respectively. It implied that MPTS molecules had been absorbed on the substrate and MPTS SAM was sequential and well-oriented compact structure. When the terminal groups (−SH) of SAM in the top-most layer to the air/silane were completely oxidized into sulfonate groups ($-SO_3H$) in 30% HNO_3 solution, the surface roughness decreased. The possible reason is that the size of sulfonate groups is bigger than the terminal groups −SH which lead to the sulfonate terminal molecules provided a more densely packed arrangement than the −SH terminal molecules. From the Fig. 1, it is seen that the surfaces of the oxidized silicon and the sulfonated MPTS-SAM are very smooth and homogeneous with R_a in the range of 0.2–0.3 nm, which is consistent with that reported elsewhere [13].

The X-ray photoelectron spectroscopic data of the surfaces were applied to detect the chemical states of some typical elements in prepared MPTS films. The changes in elemental composition can show if the reagents were deposited on the wafer surface.

The presence of SAM on silicon substrate was confirmed by XPS measurement. Fig. 2 shows XPS spectra acquired from the MPTS-coated silicon substrate. The S_{2p} signal in the spectrum for the modified silicon substrate can qualitatively account for the existence of MPTS SAM on silicon surface. The S_{2p} signal can be investigated on the films with different immersion times. The S_{2p} peak is symmetric and centered around 163.8 eV which indicated that MPTS film had been successfully obtained in our work.

With proper prehydration, the oxidized silicon substrate is capable of covalent bonding to the hydrolyzed silane molecules