



Fabrication and tribological properties of a self-assembled silane bilayer on silicon



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ABSTRACT

A self-assembled bilayer film of 1,2-bis(triethoxysilyl) ethane–octadecyltrichlorosilane (BTSE–OTS) was prepared on single-crystal silicon substrates by utilizing BTSE as an intermediate layer. The surface morphology of the film was characterized by small round protuberances, with a surface roughness of about 1.82 nm. Moreover, the BTSE–OTS bilayer film displayed comparable hydrophobicity and nano-scale friction behaviors to the OTS monolayer owing to their identical surface composition and similar surface morphology. The investigation of the micro-tribological properties revealed that the BTSE–OTS bilayer film possessed much higher anti-wear durability and load-carrying capacity than the OTS monolayer while maintaining the low friction coefficient (~0.05). The BTSE–OTS bilayer film may find expanded applications in the lubrication of micro-/nano-electromechanical systems as compared to the conventional OTS monolayer.

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1. Introduction

As a preferred kind of boundary lubricant, self-assembled monolayers (SAMs) have gained tremendous growth over the past few decades due to their effectiveness in improving the reliability and stability of the micro-/nano-electromechanical systems (MEMS/NEMSs) by reducing adhesion and friction on the surface of the devices [1,2]. Moreover, they provide the ability to tailor the tribological properties of the silicon surface at the molecular level by varying the molecular composition or structure [3,4]. Especially, the monolayers of organosilicon derivatives on silicon wafers have attracted more attention because of their superior tribological properties, among which the octadecyltrichlorosilane (OTS) SAM is the first reported one and has undergone the most extensive studies [5–7]. The OTS SAM is a densely packed and well-ordered monolayer film, covalently bound to the silicon substrate. Nevertheless, despite being known for its reputedly low friction coefficient, the OTS SAM exhibited poor anti-wear durability and load-carrying capacity due to its monolayer structure and flexibility, which will greatly limit its wider applications [8].

The mechanical durability and load-carrying capacity of the organic monolayers when subjected to a tribological load can be greatly enhanced by constructing self-assembled bilayer or multilayer films [9,10]. The formation of the layered films usually requires the molecules in the first layer of SAMs to provide reactive terminal groups capable of mediating the deposition of a second layer. Various types of self-assembled bilayer and multilayer films have been fabricated in an effort

to improve the tribological properties of the organic monolayers. However, until recently there has been little research conducted on the layered films for improving the tribological performance of the OTS SAMs. In the present paper, the 1,2-bis(triethoxysilyl) ethane (BTSE) films were firstly prepared on single-crystal silicon substrates via hydrolysis and subsequent self-assembly processes. Thereafter, the residual hydroxyl groups (—OH) on the surface of the BTSE films may play a similar role as the hydroxylated silicon substrate to further chemically adsorb another self-assembled monolayer onto the hydroxyl-terminated surface, thus making it possible to generate the BTSE–OTS bilayer films. The surface morphology, wettability, adhesive behavior and tribological properties of the as-obtained BTSE–OTS films were investigated and compared with those of the BTSE films and OTS monolayers. It is expected that the introduction of the BTSE intermediate layer would endow the BTSE–OTS films with improved tribological properties as compared to the OTS SAMs.

2. Experimental procedure

2.1. Preparation of the self-assembled films

Both BTSE (96%) and OTS (≥90%) were obtained from Sigma-Aldrich Corporation (USA) and used as received. The hydrolysis of BTSE was performed according to the procedures reported in the literatures [11,12]. Briefly, the BTSE solution was prepared in a Teflon beaker by mixing BTSE, distilled water and methanol (5:5:90 by vol.%). The pH of the silane solution was adjusted by adding acetic acid to a value of 4.5. Afterwards, the beaker was sealed and the solution was gently stirred at room temperature for 2 days to achieve a homogeneous BTSE hydrolysate.

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The P-type polished (100) Si wafers (Zhiyan Electronic Technology Co., Ltd, China) were sufficiently cleaned and then hydroxylated in a piranha solution (7:3 volume ratio of concentrated H_2SO_4 and 30% H_2O_2) at 90 °C for 30 min. After being rinsed with distilled water and dried, the wafers were immersed in the as-prepared BTSE solution for 60 s. Then, the wafers were taken out and ultrasonically washed, followed by thermal treatment at 100 °C for 1 h to generate stable BTSE films. Subsequently, the Si substrates deposited with the BTSE layers were placed in 1 mM OTS-toluene solution for 24 h under nitrogen atmosphere to allow the formation of the BTSE–OTS bilayer films. After being ultrasonically washed and dried, the substrates were heat-treated at 100 °C for 1 h. In addition, the OTS monolayer was also prepared as control by immersing the hydroxylated wafers into the OTS-toluene solution under the same conditions.

2.2. Characterization of the films

The films were characterized by X-ray photoelectron spectroscopy (XPS, Thermo ESCALAB 250Xi, USA) to analyze their chemical composition. The surface morphology of the films was observed in tapping mode with an atomic force microscope (AFM, Nanoman VS, Veeco, USA), and their surface roughness was also evaluated. The contact angles of the films were measured with a JGW-360A contact angle meter (Chenghui Testing Machine Company, China). The thickness of the films was determined by a L116-E ellipsometer (Gaertner, USA) equipped with a He–Ne laser (632.8 nm).

2.3. Evaluation of tribological properties of the films

The nano-tribological behavior of the self-assemble films was investigated at an applied normal load of 10 nN and a scanning speed of 2 $\mu\text{m/s}$ by using AFM in a contact mode. Silicon nitride cantilevers with a normal force constant of 0.3 N/m were employed. The output voltages were directly used as relative frictional force. At least five separate locations on each sample surface were measured and the average value was calculated. To obtain the adhesive force between the AFM tip and the film surface, the force–distance curve was recorded and the pull-off force was considered as the adhesive force.

The micro-tribological tests of the films were performed in a ball-on-plate contact configuration using a UMT-2MT tribometer (CETR, USA). The specimens slid reciprocally against Si_3N_4 balls ($\varphi = 4$ mm, $R_a = 0.014$ μm) at the sliding speed of 2 mm/s and the sliding distance of 5 mm. The normal load was ranged from 0.2 to 1 N. The friction coefficient-versus-time curves were recorded automatically. The surface morphology of the worn films was observed with a scanning electron microscope (SEM, S-3000N, Hitachi, Japan).

3. Results and discussion

3.1. Formation of the BTSE–OTS bilayer films

Fig. 1 schematically shows the formation process of the BTSE–OTS bilayer film on the hydroxylated single-crystal silicon wafer. Firstly, the hydrolysis of each BTSE molecule yielded six silanols ($\text{Si}-\text{OH}$). Those silanols in the adjacent BTSE molecules were capable of further condensation, forming small BTSE clusters (step 1). When the hydroxylated silicon wafer was immersed in the BTSE hydrolysate, the BTSE clusters will be chemisorbed onto the silicon substrate through the reaction between silanols and hydroxyl groups, and thus generate the stable BTSE film as the first layer (step 2). Subsequently, the OTS layer was chemically grafted to the surface of the BTSE film via the hydrolysis of the OTS molecules and the following reaction with the silanols on the other side of the BTSE clusters, eventually leading to the formation of the BTSE–OTS bilayer film (step 3).

3.2. Characterization of composition, surface morphology, thickness and contact angles

The chemical states of the elements on the surface of the films were detected by XPS. It was observed in Fig. 2 that, the three types of films displayed almost the same chemical compositions because the deposition of the OTS layer on the BTSE film did not introduce any new elements. However, the BTSE–OTS films exhibited an enhanced intensity of the carbon element as compared to both BTSE and OTS monolayers (inset of Fig. 2), which could be induced by the increase in the C carbon content with the self-assembly of the OTS molecules as the second layer. Furthermore, no peaks related to the chlorine element were detected in the spectrum of the BTSE–OTS films, indicating that the trichlorosilane groups of the OTS molecules reacted completely with the hydroxyl groups on the BTSE films.

The AFM images of the silicon substrate and different types of self-assembled films were displayed in Fig. 3. Their surface roughness (R_q) was also calculated from the entire 5×5 μm^2 area of the images and listed in Table 1. It was observed in Fig. 3a that the bare silicon substrate exhibited a quite smooth surface. However, after deposition of the BTSE films on the Si substrates, the surface was characterized by a grainy topography due to the homogeneous formation of the BTSE nano-clusters (Fig. 3b), with the surface roughness of about 1.31 nm. Furthermore, the chemical absorption of the OTS layers onto the BTSE films resulted in a surface that was covered with some round protuberances (Fig. 3c). It was quite similar to the surface morphology of the OTS monolayer shown in Fig. 3d, indicating that the OTS self-assembled film was formed on the BTSE layer. Additionally, the surface roughness of the BTSE–OTS bilayer films was estimated to be 1.82 nm over an area of 5×5 μm^2 , which was slightly higher than 1.68 nm of the OTS

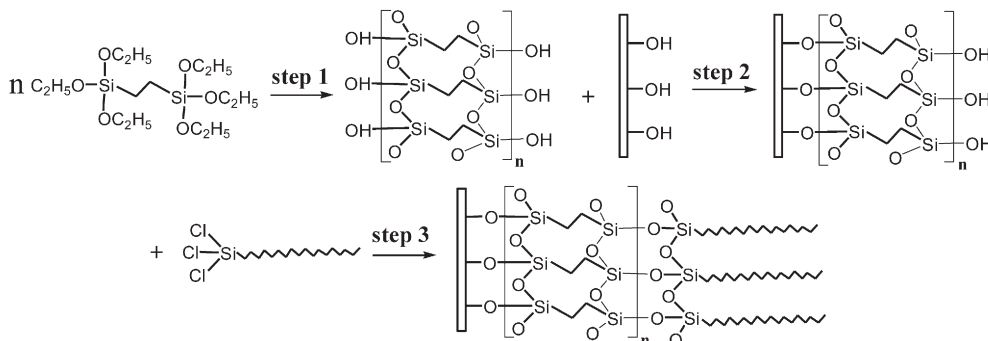


Fig. 1. Schematic drawing of the formation of the BTSE–OTS films on hydroxylated silicon wafers.

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