Wear 332-333 (2015) 879–884

Contents lists available at ScienceDirect

Wear

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

Effect of coadsorption of water and alcohol vapor on the nanowear of silicon

L. Chen [a], Y.J. Yang [a], H.T. He [a], S.H. Kim [b], L.M. Qian [a,*]

[a] Tribology Research Institute, National Traction Power Laboratory, Southwest Jiaotong University, Chengdu 610031, China
[b] Department of Chemical Engineering and Materials Research Institute, Pennsylvania State University, University Park, PA 16803, USA

ARTICLE INFO

Article history:
Received 15 September 2014
Received in revised form
21 January 2015
Accepted 13 February 2015

Keywords:
Tribochemical wear
Silicon
Coadsorption
Water
Alcohol

ABSTRACT

Using an environment-controlled atomic force microscope, the nanowear of silicon against SiO_2 microsphere was investigated under various relative humidity (RH) and ethanol partial pressure (P_a/P_{sat}) conditions. When RH was below 10%, there was no discernable wear of the substrate in any P_a/P_{sat} conditions. However, when RH $>$ 10%, although the contact pressure (1.3 GPa) was far less than the yield stress of silicon material (7 GPa), the occurrence of tribochemical wear was observed on silicon surface without ethanol adsorption. When ethanol vapor was introduced, the wear of silicon was inhibited fully or partially depending on RH. At RH below 50%, there was a critical ethanol partial pressure above which tribochemical reaction was completely suppressed and no wear was generated on silicon surface. At RH above 50%, the wear of silicon could be significantly reduced, but not completely, with the increase of ethanol partial pressure. Upon addition of ethanol vapor, the frictional energy dissipation decreased and the energy barrier for tribochemical reaction could also become larger. These factors could explain the lubrication effect of the adsorbate ethanol layer in humid environment. The RH and ethanol partial pressure conditions for the lubrication of Si/SiO_2 sliding pairs were identified, which can be used for optimizing the MEMS operation conditions without failure due to wear.

1. Introduction

Microelectromechanical systems (MEMS) with a characteristic length of 100 nm–1 mm have been successfully employed in military and commercial fields [1–3]. Silicon has been widely used as a main construction material of MEMS due to its excellent properties in lithographic microfabrication and micromachining techniques [4,5]. As the dimensions of moving parts shrink to micro/nanometer scale, the surface force of tribological interface plays important roles owing to the large ratio of surface area to volume [6]. In this situation, the dynamic moving parts can fail because of serious tribological problems such as high friction and serious wear, which greatly restrict the reliability of MEMS [7–10]. Therefore, understanding and control of the nanowear of silicon is an important issue of concern.

Silicon does not have any intrinsic lubrication properties, so it is subject to significant wear during sliding processes. When the contact pair is chemically inert (such as diamond tip), the mechanical wear of silicon surface usually occurs under high contact pressure [11,12]. However, when the contact pair is chemically reactive (such as Si or SiO_2 tip), serious tribochemical wear of silicon may occur in humid air under a contact pressure far below its yield stress (7 GPa) [13–15]. Such tribochemical wear was also observed in silicon-based MEMS devices [7–10]. To prevent the wear of silicon, various methods have been attempted including the deposition of hard coating or hydrophobic organic film, such as diamond-like carbon (DLC) coating and self-assembled monolayers (SAMs), and so on [1,16–19]. However, the conformal coating of DLC inside deep gaps or trenches between high asperity objectives is difficult. The poor durability of SAMs also limits their practical applications in MEMS [20].

Recent experimental results indicated that both the mechanical wear and tribochemical wear of silicon material can be effectively prevented in an alcohol vapor environment [21,22]. This method has been successfully used for the lubrication of MEMS devices to extend their lifetime [23,24]. Previously, most studies focused on the alcohol lubrication at water-free conditions. Actually, it is difficult to completely eliminate the water vapor in the dynamic MEMS devices. The existence of water molecules would affect the adsorption state of alcohol layer and could deteriorate the alcohol lubrication [25,26]. In the case of mixed vapor of water and alcohol, the binary adsorbate layers present in a layered structure, in which alcohol is at the adsorbate/vapor interface and water is inside the adsorbate layer [25]. The thickness and structure of the binary layers would change depending on the composition of water and alcohol [25,28]. Through a MEMS side-wall tribometer, Barnette et al. [26] investigated the effect of water vapor on the

---

* Corresponding author. Tel.: +86 28 87600687; fax: +86 28 87603142.
E-mail address: Linmao@swjtu.edu.cn (L.M. Qian).

http://dx.doi.org/10.1016/j.wear.2015.02.052
0043-1648/

alcohol lubrication at a fixed alcohol partial pressure ($P_a/P_{sat}=50\%$). They found that the full coverage of alcohol layer could effectively prevent the silicon wear. However, the increase of relative humidity (RH) reduced the amount of alcohol adsorbed at the interface and eventually led to the failure of MEMS device operation at RH above 30% [26]. It was reported that the coverage of adsorbate alcohol layer would be less than monolayer on silicon surface at relatively low P_a/P_{sat} [27,28]. Therefore, it is important to verify whether the partial coverage of adsorbate alcohol layer can prevent the wear of silicon under relatively low RH and P_a/P_{sat} conditions. Moreover, to better achieve the lubrication of silicon-based MEMS, it is essential to investigate the effect of water vapor on the alcohol vapor lubrication at various partial pressures.

In this paper, the wear behavior of single-crystalline silicon rubbed against a SiO_2 microsphere was investigated at various RH and ethanol partial pressure conditions. It was found that the nanowear of silicon strongly depended on the coadsorption of water and ethanol vapors. At RH below 50%, the silicon wear could be completely prevented depending on the ethanol partial pressure (P_a/P_{sat}). However, when RH was higher than 50%, the surface damage on silicon surface was only partially suppressed under all ethanol partial pressure conditions tested in this study. The results suggest that the ethanol vapor lubrication is suitable as a protecting method in MEMS applications at RH $\leq 50\%$ and relatively high P_a/P_{sat}.

2. Material and methods

The p-doped Si(100) wafers were purchased from MEMC Electronic Materials, Inc. By using an atomic force microscope (AFM, SPI3800N, Seiko, Japan), the root-mean-square (RMS) roughness of the Si(100) wafers were measured to be 0.06 ± 0.01 nm over a 500 nm × 500 nm area. The native oxide layer was retained on the silicon surface to simulate the real contact surface in MEMS, whose thickness was determined by Auger Electron Spectroscopy (AES) as ~0.5 nm [29]. Before wear tests, the silicon wafers were ultrasonically cleaned in methanol, ethanol, and deionized water for 10 min in turn.

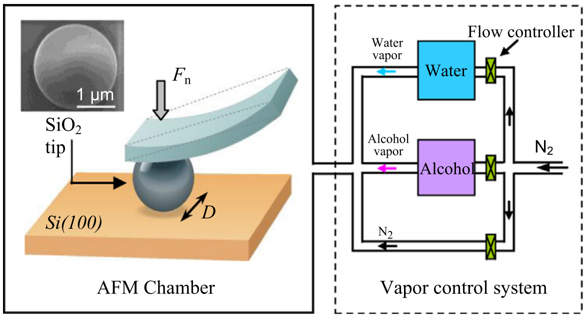

Fig. 1. The schematic illustration showing the wear tests operated in AFM with an atmosphere chamber (left part) connected an external vapor control system (right part). A SiO_2 microsphere (scanning electron microscope image shown in the inset) moves horizontally on the silicon surface with a stroke $D=500$ nm under a normal load $F_n=3$ μN. With the atmosphere controlling system, the relative humidity can be controlled in 0–80% and the P_a/P_{sat} in AFM chamber can be controlled in 0–100% with the error of ±2%.

As shown in Fig. 1, all the wear tests and topography imaging were performed by the AFM equipped with an atmosphere chamber connected an external vapor control system. Environments mixed by water and ethanol vapors were realized by a vapor control system (dashed box in Fig. 1). Before filled with mixture vapor, the AFM chamber was pumped down to $\sim 5 \times 10^{-4}$ Torr to achieve low moisture condition. The N_2 lines passed through two bottles filled with water/glass beads and ethanol/glass beads, and finally joined into a single inlet line. The partial pressures relative to the saturation pressure (P/P_{sat}) of water or ethanol could be controlled by varying the flow rates of dry, water-saturated, and ethanol-saturated N_2 gas streams through this system. More details about this method have been described in previous literature [30].

The wear tests were operated by using SiO_2 spherical tips, which were purchased from Novascan Technologies, USA. Each SiO_2 tip consisted of a SiO_2 microsphere with a radius of ~1 μm (inset in Fig. 1) attached to a silicon cantilever whose spring constant was calibrated to be in the range of 10.5–13.8 N/m [31]. During the wear tests, the sliding speed was 1 μm/s, the sliding stroke (D) was 500 nm, the applied normal load (F_n) was 3 μN and the number of sliding cycles (N) was 200. After the tests, the topography of the wear area of the silicon surface was imaged using a sharp silicon nitride probe (MLCT, Veeco, USA), which had a tip radius of 10–20 nm and a nominal spring constant of 0.1–0.3 N/m. The coadsorption of ethanol and water was measured with a Thermo Nicolet Nexus 670 infrared spectrometer with an attenuated total reflectance infrared spectroscopy (ATR-IR) setup; more details of the experiments could be found elsewhere [25,28].

3. Results

3.1. Coadsorption of water and ethanol on silicon surface

The main driving force for adsorption of ethanol molecules to the silicon surface is the formation of hydrogen bonds between the surface hydroxyl and ethanol OH groups [27]. In the conditions of water and alcohol mixture vapor, the hydroxyl group of alcohol is hydrogen bonded to the water molecule underneath. The adsorbed layer of water and alcohol assumed a binary layers structure [25,28]. To confirm the coadsorption of water and ethanol on silicon surface,

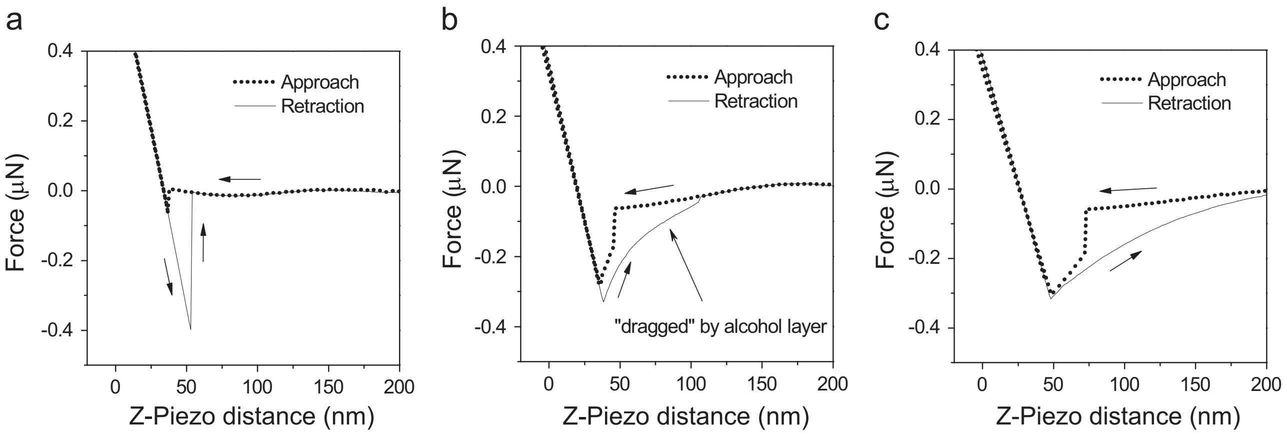

Fig. 2. Force–distance curves of Si(100)/SiO_2 pair at RH=30%. (a) $P_a/P_{sat}=0\%$, (b) $P_a/P_{sat}=20\%$, (c) $P_a/P_{sat}=40\%$.