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# Threshold contact pressure for the material removal on monocrystalline silicon by $SiO_2$ microsphere

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ABSTRACT

By using an atomic force microscope, the nanowear tests of Si(100) surface against $SiO_2$ microsphere were performed both in humid air and in water. The experimental results indicated that mechanical interaction could significantly enhance the tribochemical wear of Si/$SiO_2$ pair. There existed a threshold pressure (~1.1 GPa) for tribochemical wear under one sliding cycle at 50% RH, which was much less than the mechanical threshold pressure (~10.9 GPa) for the initial yield of Si(100). When the wear tests were performed in water, such threshold pressure can be further reduced to less than 0.28 GPa. The reason can be explained to the facilitative tribochemical reaction in water, which was induced by the formation of more Si–O–Si bonding bridges and rupture of more Si-Si networks. Meanwhile, when the number of sliding cycles increased to 70, the threshold pressure of Si/$SiO_2$ pair at 50% RH can also be reduced to 0.28 GPa, which may be attributed to the accumulation of residual energy within the contact area. The results may help us optimize the tribological design of dynamic MEMS and realize the high-precision polishing process under ultralow pressure.



## 1. Introduction

As an excellent structural material, monocrystalline silicon has been widely used in microelectromechanical systems (MEMS), such as micropumps, micromixers, and so on [1,2]. However, the wear failure of dynamic MEMS has become a critical issue, which strongly limits the service lives of MEMS, especially in humid air and water due to serious tribochemical reaction [3–5]. A planar, smooth and damage-free silicon surface by chemical mechanical polishing/planarization (CMP) process is required in all above products manufacturing [6–8]. Therefore, deeper understanding in the controllable silicon material removal can not only optimize the reliable operations of MEMS, but also provide useful knowledge for nanopolishing of silicon.

In previous studies, the surface wear was strongly influenced by many factors, such as the physical and chemical properties of the sliding interfaces, surface treatments and environment effects, and so on [9–12]. The mechanical interaction played a crucial role in the tribochemical removal process [13]. When the imposed energy is large enough to overcome the energy barrier of tribochemical reaction, the tribochemical wear on silicon surface would be activated by the interfacial mechanical interaction [9]. The imposed energy depends on the mechanical action and has a positive correlation with the contact pressure [14,15]. Investigation of the threshold contact pressure can not only help determine the energy barrier of tribochemical reaction under the given conditions, but also understand the tribochemical wear mechanism of silicon. In addition, during a typical tribochemical removal process of CMP, contact pressure presented one of the key factors to affect both polishing rate and surface quality [6]. For example, Zhang et al. reported that high applied pressure may produce thick damage layer with amorphous phase transformation and oxidation beneath silicon surface [16]. Xu et al. indicated that the surface quality of polished surface could be significantly improved by decreasing applied pressure, namely that the surface roughness of polished surface could decrease from 0.45 nm to 0.2 nm when the applied pressure decreased from 125 kPa to 25 kPa [17]. Therefore, to make a deeper understanding on wear mechanism of silicon and obtain high quality of polished surface, it is essential to investigate the threshold value of contact pressure for the tribochemical wear of Si/$SiO_2$ interface.

Using atomic force microscope (AFM), a large amount of nanoscale wear tests have been conducted to investigate various aspects of nanotribology, nanomechanics and materials characterization [18–20]. Bhushan et al. [21] and Yu et al. [13] reported that mechanical interaction played a dominant role in the mechanical wear behaviors of silicon surface rubbed by diamond tip. With the increase in applied normal load, the scratch damage on Si

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(100) surface would experience the following three stages: formation of surface hillock, generation of groove and material removal as the plastic flow. The critical contact pressure for plastic deformation of Si(100) was estimated as 10.9 GPa, which was close to the hardness value of Si(100) (11–13 GPa) [13,22]. Recent nanoscale experimental results indicated that the threshold stress for the material removal of silica would decrease due to the stress corrosion reactions of silicate network under the presence of water and shear stress [23]. The nanowear of Si/$SiO_2$ tribopair in humid air demonstrated that serious damage would be induced by the chemical reaction involving water even when the contact pressure was less than 1 GPa [24,25]. However, no available literature was found to report on the study of threshold contact pressure for the tribochemical removal of Si/$SiO_2$ interface.

In this paper, the threshold contact pressure for material removal of Si(100) surface against $SiO_2$ microsphere was studied at 50% RH and in water by an AFM. The results showed that the threshold contact pressure for material removal of Si/$SiO_2$ pair prominently decreased to 1.1 GPa at 50% RH and further decreased to less than 0.28 GPa in water. The effect of water content and wear cycles on the threshold contact pressure was discussed. The results may help us optimize the tribological design of dynamic MEMS and realize the high-precision polishing process under ultralow pressure.

## 2. Materials and methods

The nanowear test samples are p-doped Si(100) wafers (MEMC Electronic Materials, Inc., USA) with a native oxide layer of ~0.5 nm in thickness [26]. With an AFM (SPI3800N, Seiko, Japan), the root-mean-square roughness of silicon wafer was measured as no more than 0.5 nm over an area of 5 μm × 5 μm [27]. To eliminate the effect of the native oxide layer on the material removal of silicon substrate, the silicon wafers were dipped in 5 wt% hydrofluoric acid (HF) solution for 2 min to remove the oxide layer. Before the tests, the samples were ultrasonically cleaned with acetone, ethanol and deionized water for 3 min in sequence to remove surface contamination [28]. Moreover, each nanowear test was controlled within 30 min to avoid the influence of growing native oxide on the wear tests.

As shown in Fig. 1, a $SiO_2$ microsphere with a radius of ~1 μm suspended on a silicon cantilever was used to simulate the single asperity contact at Si/$SiO_2$ interface. Through a standard cantilever with a spring constant of approximately 3.438 N/m (CFFC-NOBO, Veeco, USA), the spring constant of silicon cantilever was calibrated to be in the range of 16.8–19.7 N/m. For the applied normal load $F_n$ of 0.05–5 μN and adhesion force (pull-off force) of ~0.05 μN, the maximum contact pressure $P_{max}$ of the Si/$SiO_2$ contact area was calculated to be less than 1.5 GPa in entire experimental process based on the Derjaguin–Muller–Toporov (DMT) contact mechanics [29]. During the nanowear tests, the displacement amplitude $D$ was 500 nm, the sliding speed $v$ was 2 μm/s and the temperature was controlled at 23 ± 2 °C. The friction force was calibrated by a modified wedge method using a silicon grating with a wedge angle of 54°44′ (TGF11, Mikro Masch, Germany) [30]. The relative humidity (RH) was controlled by a home-built atmosphere chamber connected to an external vapor control system. Further details on the system composition and experimental process could be found in the previous literatures [25,31]. The nanowear tests on silicon wafers in water were performed by a self-developed liquid cell. The deionized water with a conductivity of 0.5 μs/cm was obtained from a laboratory water purification system (Mater-S15, Hi-tech, China). After the wear tests, sensitive silicon nitride tips (MLCT, Veeco, USA) with curvature radii of 10–20 nm and nominal spring constant of ~0.1 N/m were used to scan the wear area on silicon surfaces. The scan size of the AFM image was 1 μm × 1 μm. Before imaging, the AFM chamber was pumped into ~$5 \times 10^{-4}$ Torr vacuum to avoid the influence of adsorbed water film on samples. The subsurface atomic structure of Si(100) wear tracks formed after the nanowear test at 50% RH and in water were detected by the cross-sectional transmission electron microscope (XTEM, Tecnai G2 F20, FEI, USA). An epoxy polymer passivation layer was deposited on the silicon surface to protect the wear area from the damage by subsequent focused ion beam milling (FIB, NanoLab 400, FEI, USA).

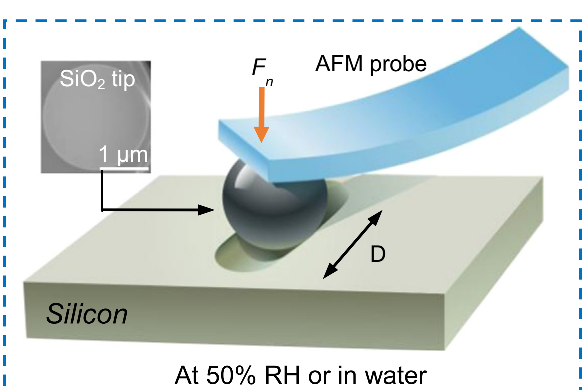


**Fig. 1.** Schematic diagram showing the nanowear test between $SiO_2$ tip and silicon samples by AFM equipped with humidity-controlled chamber and self-developed liquid cell.

## 3. Experimental results

### *3.1. Threshold contact pressure for the material removal on silicon by $SiO_2$ spherical tip at 50% RH*

Previous work suggested that silicon material can be removed by sliding $SiO_2$ tip under much lower contact pressure because of the tribochemical wear [13,25]. To explore the lowest contact pressure for the tribochemical reactions on silicon surface in humid air, a $SiO_2$ spherical tip with a radius of ~1 μm was used in the nanowear test under the normal loads of 0.05–5 μN. Figs. 2 and 3 show the topographic images and the average depths of wear scars on silicon surfaces after rubbed with a $SiO_2$ microsphere under various sliding cycles and contact pressures at 50% RH. As shown in Fig. 2, there existed a threshold pressure for material removal under different sliding cycles at 50% RH, all of which were much less than the mechanical threshold pressure of Si(100) in dry condition (~10.9 GPa). When the wear tests were performed for only one sliding cycle, there was no discernable damage within the spatial resolution of AFM at low contact pressure. As the contact pressure increased to 1.1 GPa, material removal was initiated on silicon substrate. When the number of sliding cycles in nanowear test was set at 50 and 70 (those images are not presented in Fig. 2), the threshold pressure for the material removal was decreased to 0.49 and 0.28 GPa, respectively. As shown in Fig. 2, the wear behaviors on silicon surface exhibited a transition from wearless states to severe wear with the increase in contact pressure and sliding cycle. Moreover, there was a partial wear transition between above two periods, where the material removal did not happen in the whole sliding area. For example, the wear scars showed intermittent material removal behavior when the number of sliding cycle was 5 and the contact pressure was in the range of 0.79–0.97 GPa. The special wear behavior may be attributed to a randomness of the tribochemical reaction, which means that the silicon atomic has a certain probability to be removed by sliding $SiO_2$ microsphere in this case. The continuous grooves were