

Humidity Dependence of Tribochemical Wear of Monocrystalline Silicon

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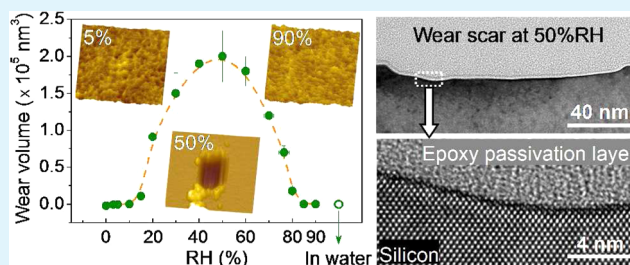
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Supporting Information

ABSTRACT: The nanowear tests of monocrystalline silicon against a SiO₂ microsphere were performed using an atomic force microscope in air as a function of relative humidity (RH = 0%–90%) and in liquid water at a contact pressure of about 1.20 GPa. The experimental results indicated that RH played an important role in the nanowear of the Si/SiO₂ interface. In dry air, a hillock-like wear scar with a height of ~0.4 nm was formed on the silicon surface. However, with the increase of RH, the wear depth on the silicon surface first increased to a maximum value of ~14 nm at 50% RH and then decreased below the detection limit at RH above 85% or in water. The transmission electron microscopy analysis showed that the serious wear on the silicon surface at low and medium RHs occurred without subsurface damage, indicating that the wear was due to tribochemical reactions between the Si substrate and the SiO₂ counter surface, rather than mechanical damages. The RH dependence of the tribochemical wear could be explained with a model involving the formation of “Si—O—Si” chemical bonds (bridges) between two solid surfaces. The suppression of tribochemical wear at high RHs or in liquid water might be attributed to the fact that the thickness of the interfacial water layer is thick enough to prevent the solid surfaces from making chemical bridges. The results may help us understand the nanowear mechanism of silicon that is an important material for dynamic microelectromechanical systems.

KEYWORDS: nanowear, tribochemistry, relative humidity, monocrystalline silicon



1. INTRODUCTION

Silicon-based microelectromechanical systems (MEMS) offer great promise for developing micromotor, accelerometer, microbearing systems, and so on.^{1–4} However, the wear of the contact interfaces of silicon has become one of the major concerns in dynamic MEMS devices.^{2–4} For reliable operations of MEMS in ambient air, it is essential to understand the wear process of silicon as a function of relative humidity (RH) and develop wear-resistant approaches.

In the past, micro/nanowear experiments of silicon in humid air were performed with diamond tips because of their excellent hardness and wear-resistance.^{5–7} Using a pin-on-disk tribometer, Xu and Kato⁵ investigated the wear behavior of silicon against a diamond pin at RH = 1.2%, 24%, and 80%. They reported that the wear of silicon was dominated by the mechanical microcutting, and no tribochemical wear was involved. Using an atomic force microscope (AFM), Bhushan and Goldade⁶ researched the nanowear of silicon against a diamond tip at RH = 0% and 80%. They also reported that the mechanical interaction dominated the wear process of silicon. When the contact pressure was 7.4 GPa, the silicon substrate showed a hillock-like protrusion at 0% RH, but no surface damage at 80% RH.⁶

However, the mechanical wear of silicon by diamond tip^{5–7} cannot provide critical insights relevant to the performance of

silicon-based dynamic MEMS devices in humid air since these devices involve sliding of Si against Si or SiO₂ surfaces.⁸ Chung and Kim⁹ performed the wear tests of a silicon AFM tip on a silicon surface in humid air. With the increase of RH (RH = 20%, 40%, and 60%), the wear volume of the silicon tip increased. They attributed this to the increase of adhesion force.⁹ Only a few papers discussed the tribochemical process of silicon under different humid conditions. Yu et al.¹⁰ presented the nanowear of a silicon (100) surface against an SiO₂ AFM tip at RH = 0%–50%. They indicated that the nanowear of silicon would be aggravated by the increase of RH due to the effect of interfacial tribochemistry. Under dry atmosphere, the silicon surface can resist mechanical wear, regardless of the counter-surface chemistry and ambient gas type, as long as the contact pressure is lower than the yield stress of silicon.^{7,10} With the increase in the RH of humid air from 0% to 50%, the damage mode of the Si/SiO₂ interface changed from weak mechanical deformation (protrusion) to serious tribochemical wear (material loss) even at a contact pressure (1.38 GPa) much lower than the yield stress (7 GPa).¹⁰ However, when the wear tests of the Si/SiO₂ interface were conducted in liquid

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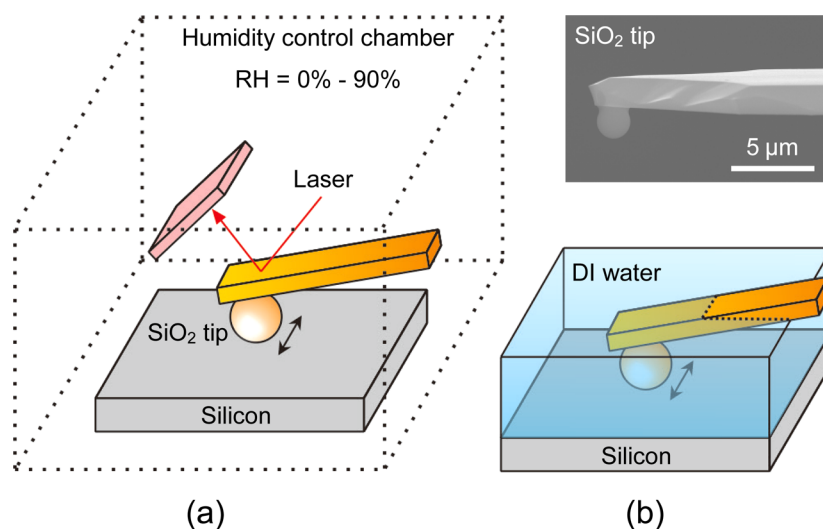


Figure 1. Illustration showing the wear tests of Si/SiO₂ interface by AFM in a humidity control chamber (a) and in water (b). The top-right inset shows a scanning electron microscope (SEM) image of a typical SiO₂ tip used in the wear tests.

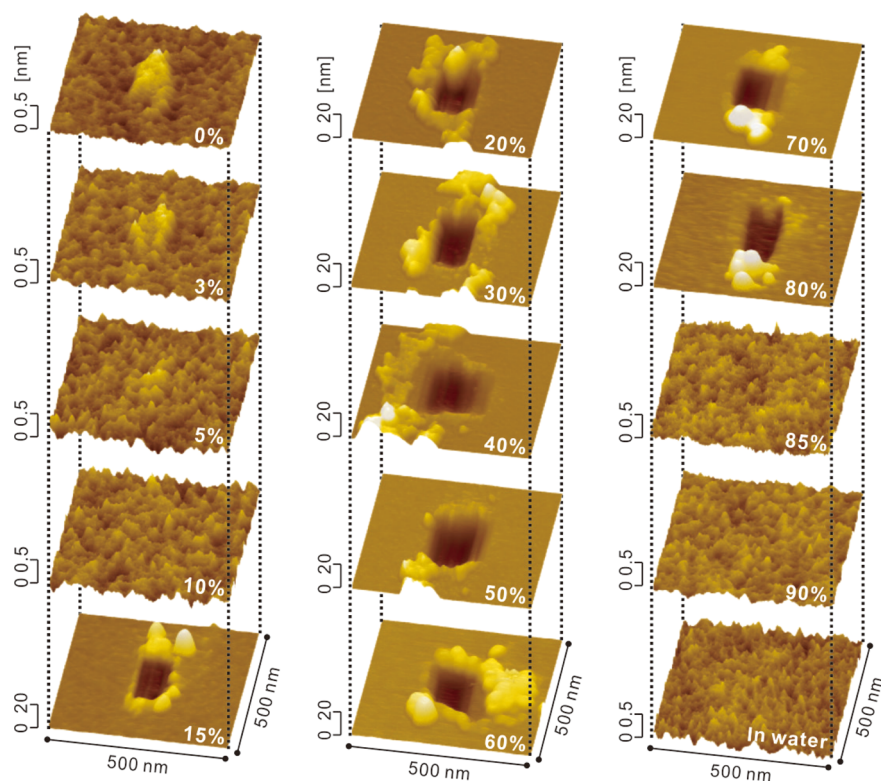


Figure 2. AFM images of wear scars on silicon surface at various RHs and in water. $F_n = 3 \mu\text{N}$, $L = 200 \text{ nm}$, $v = 2 \mu\text{m/s}$, and $N = 200$ cycles. Note the height full-scales for wear scars at RH = 15–80% are 20 nm, and all others are 0.5 nm.

water under the same loading condition, the tribochemical wear was suppressed, and no discernible material loss was observed on the silicon surface.¹¹ It is clear that the presence of water in the surrounding environment does not always facilitate the tribochemical wear of silicon. Therefore, it is essential to understand the tribochemical wear behavior of crystalline silicon over the full humidity range and in liquid water.

In the present study, the nanowear of a silicon wafer (covered by a native oxide layer) against a SiO₂ tip was performed using an AFM in an RH range from 0% to 90% as well as in liquid water. The correlation between the dissipated energy and the wear of silicon sample at various RHs was

discussed. The tribochemical wear on the silicon surface was verified by the transmission electron microscopy (TEM) analysis of the wear area. The experimental findings of this work will be helpful to elucidate the wear mechanism of silicon in humid air and optimize the tribological design of dynamic MEMS working in humid conditions.

2. MATERIALS AND METHODS

Figure 1 schematically illustrates the experimental setup. A p-doped Si(100) wafer with a thickness of 0.5 mm was purchased from MEMC Electronic Materials, Inc., U.S.A. The AFM used in this study was a Seiko SPI3800N system that can be operated in vacuum as well as in

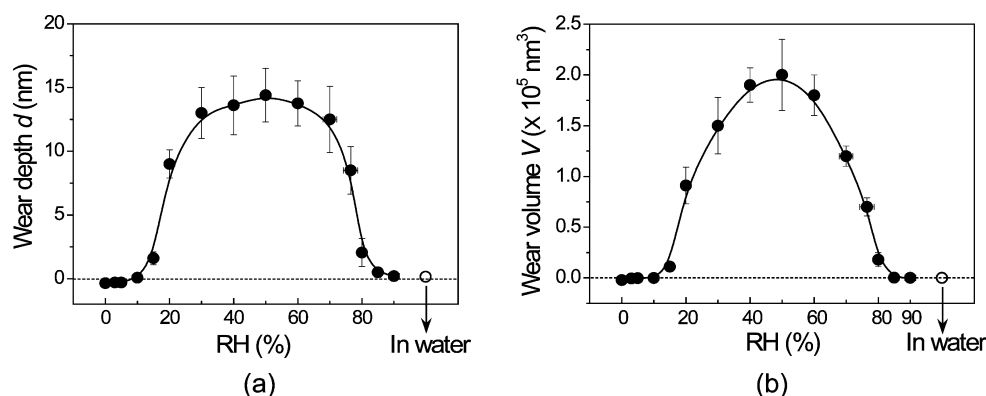


Figure 3. Effect of RH on the wear depth d (a) and wear volume V (b) on silicon surface. Both the values of d and V under the same loading conditions in water were also plotted as comparison.

ambient pressure. Topographic imaging of pristine wafers with a silicon nitride AFM tip (curvature radius = 20 nm; spring constant = 0.1 N/m; MLCT, Veeco, U.S.A.) found the root-mean-square (RMS) roughness of the silicon wafer to be 0.07 nm over a $500 \times 500 \text{ nm}^2$ area.¹¹ To simulate dynamic processes of silicon-based MEMS devices, the native oxide layer on the Si(100) surface was not removed. The native oxide thickness was found to be about 0.5 nm from an Auger electron spectroscopy analysis (AES, PHI700, ULVAC-PHI, Japan, see Figure S1 in the Supporting Information, SI). The thickness of the native oxide layer on silicon sample did not vary with the modification of the RH, as shown in SI Figure S1. The wear tests were conducted with spherical SiO_2 tips with a radius (R) of 1 μm (Novascan Technologies, U.S.A.; SEM image is shown in the inset). Through the thermal excitation method,¹² the normal spring constant (k) of the cantilever of SiO_2 tips was calibrated as about 12 N/m. If not specially mentioned, the normal load F_n applied to the SiO_2 tip was set at 3 μN . The friction force was calibrated by a modified wedge method using a silicon grating with a wedge angle of $54^\circ 44'$ (TGF11, Mikro Masch, Germany).¹³ The wear tests of silicon sample surface against SiO_2 tip (Si/SiO_2 interface) were performed in a humidity-controlled chamber at various RHs (0–90%), as shown in Figure 1(a). The RH was measured with a RH meter (HP22-A, Rotronic, Switzerland) positioned ~ 5 cm from the sample surface. The RH at the beginning and end of wear test was recorded to ensure the variation of RH value within 1% for the given RH lever. The wear tests in deionized (DI) water were carried out using a liquid cell, as shown in Figure 1(b). The DI water was purified by a laboratory water purification system (Master-S15, Hi-tech, China). The pH value of DI water at room temperature was 6.5 and its conductivity was 0.5 $\mu\text{S}/\text{cm}$. Before the wear tests in water, the cantilever holder, the liquid cell, and the silicon sample were thoroughly cleaned to ensure the cleanness of system.¹⁴

On the basis of the DMT contact mechanics and the adhesion force F_a measured in humid air and in water (see Figure S2 in the SI), the maximum contact pressure P_c in the Si/SiO_2 contact area was estimated to be 1.12–1.20 GPa.¹⁵ Under these contact pressures, the elastic indentation depth of the silicon surface would be ~ 1.3 nm. The sliding span L was 200 nm, and the sliding velocity v was 2 $\mu\text{m}/\text{s}$. The number of wear cycles N varied from 1 to 200. After the nanowear tests, the topography of wear scars was scanned with the silicon nitride tip in a contact mode in vacuum. The scan size of the AFM images was $500 \times 500 \text{ nm}^2$.

To understand the wear mechanism of the Si/SiO_2 interface in humid air, a transmission electron microscope (TEM, Tecnai G2 F20, FEI, U.S.A.) was used to characterize the subsurface atomic structure of the silicon wear track formed after the wear test at RH = 50%. During the wear process, the contact pressure was ~ 1 GPa, the scratching velocity v was 24 $\mu\text{m}/\text{s}$ and the number of wear cycles was 200. The cross-sectional TEM sample was prepared using a focused ion beam miller (FIB, Nanolab Helios 400S, FEI, Holland). For the sample preparation, an epoxy polymer, instead of platinum, was deposited on silicon sample surface as the passivation layer, because

the decrystallization of silicon could occur during the platinum deposition.

3. EXPERIMENTAL RESULTS

3.1. Wear of Silicon at Various RHs and in Water. In order to investigate the effect of RH on the wear of silicon, the wear tests of the Si/SiO_2 interface were carried out at a normal load of 3 μN , where the maximum contact pressure did not exceed 1.20 GPa.¹⁵ The topography of wear scars made after 200 cycles of sliding was shown in Figure 2. A plot of wear depth (d) versus RH is shown in Figure 3(a). When the wear test of the Si/SiO_2 interface was performed in dry air, a hillock-like wear scar (protrusion) with a height of ~ 0.4 nm was formed in the scratch area of the silicon surface. When water vapor was introduced into the environmental chamber, the hillock-like protrusion disappeared and no discernible wear of the silicon surface was observed at RH = 10%, as shown in Figure 2. With the further increase of RH, the groove-like wear scar (trench) was formed on the silicon surface. The wear depth increased quickly from ~ 1.5 nm at 15% RH to ~ 13 nm at 30% RH and then reached the maximum value of ~ 14 nm at 50% RH. As RH increased further, the wear depth gradually decreased to ~ 12.5 nm at 70% RH and then dramatically dropped to ~ 2 nm at 80% RH. Finally, when the wear tests were conducted at RH above 85% and in liquid water, no discernible surface damage was observed on the silicon surface. It was noted that the depth of the nanowear scar decreased while the value of the adhesion force increased in the RH region of 50–70%, as shown in Figures 2 and 3 and SI Figure S2. Therefore, the adhesion force does not seem to be a main determinant governing the RH dependence of the nanowear behavior of Si/SiO_2 (see Figure S2 in the SI); the nanowear seemed to be dominated by the structure and thickness of the adsorbed water layer on the surface of silicon sample.¹⁰

The wear volume V (Figure 3(b)) was proportional to the square of the wear depth d (see Figure S3 in the SI). When the sliding span is fixed, the wear volume will be proportional to the cross-section area of the wear scar, which is in turn a function of the wear depth. As a result, the V – d curve can be well fitted by a second-order equation.

3.2. Dependence of Wear Rate on the Frictional Energy Dissipation. Generally, the wear of material depends on the dissipated energy during the interfacial sliding. One may expect more serious mechanical wear when more energy is dissipated through friction.^{16,17} The tribochemical wear may also become severe at higher friction if a fraction of the energy

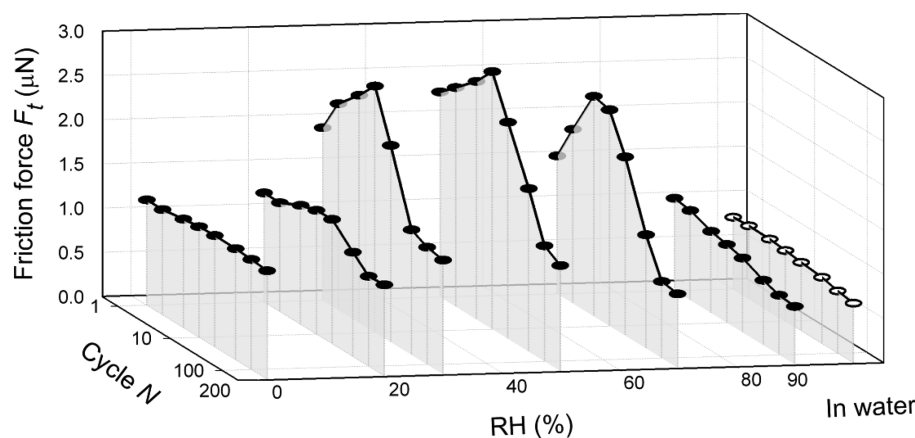


Figure 4. F_t - N -RH curves of the Si/SiO₂ interface under the normal load of 3 μ N.

dissipated by friction is used to overcome the activation energy of bond dissociation.^{18–20} To understand the humidity dependence of the Si/SiO₂ wear, the correlation between the wear rate and frictional energy dissipation was analyzed.

Since the dissipated energy was the integration of the friction force, F_t , over the total sliding distance,^{16,17} the friction force of the Si/SiO₂ interface at various RHs was measured. Figure 4 plotted the friction force (F_t) vs the number of cycles (N) measured at various RHs and in water. At RH = 0% (dry air) and >80% (high humidity) as well as in liquid water, the friction force was stable during the entire wear process (200 cycles), and no discernible wear was observed on the silicon surface (Figure 2). However, in the intermediate RH range between 20% and 80%, the friction force F_t increased during the initial 10 cycles and then decreased to a stable value as the sliding cycle continued. Meantime, serious wear occurred on silicon surface, as shown in Figure 2. Clearly, there was a direct correlation between the variation of friction force with wear cycle and the total wear volume of silicon surface in humid air (see Figure S4 in the SI).

The RH dependences of F_t in the initial cycle and at the final steady state (see Figure S5 in the SI) indicated that the chemical and/or physical conditions of the interfaces dynamically changed over time.²¹ The increase of initial friction at the low RH condition could be explained as the growth of a “solid-like” structured layer of water on the silicon substrate covered with the native oxide layer.¹⁰ With the increase in wear cycle, the transition to low friction occurred after the removal of native oxide layer of the silicon wafer by tribochemical wear.²¹ After removal of the native oxide during this high-friction run-in period, the wear rate decreased.²¹

Figure 5 compares the correlation between the total dissipated energy E and the averaged wear rate γ of the Si/SiO₂ interface over 200 sliding cycles at various RHs. Here, the wear rate γ was determined by dividing the total wear volume with the frictional work.¹⁰ In general, the dissipated energy over 200 sliding cycles showed a trend similar to the wear rate of silicon substrate at RH >20%.²¹ It was reported that when the silicon surface was terminated by hydroxyl, the activation energy for the hydrolysis of the surface Si—O—Si bond would be about 113.8 kJ/mol.²² At the sliding interface, the activation energy could be lower with the help of mechanical shear stress.^{21,22} In any case, if the imposed energy is high enough to overcome this activation barrier, then the tribochemical reaction could happen. The result shown in Figure 5 suggested

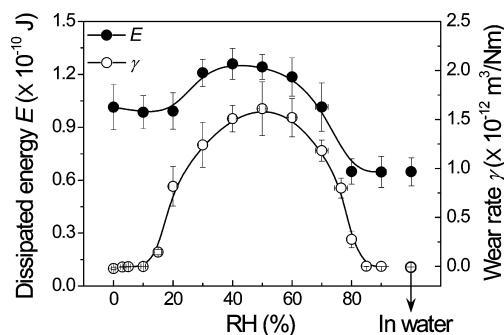


Figure 5. Correlation of dissipated energy E and wear rate γ on silicon surface at various RHs.

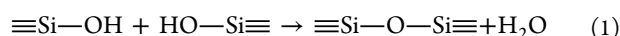
that when the wear test was performed at RH > 80% or in water, the frictional energy at the sliding interface might not be high enough to induce the tribochemical damage to the silicon surface.

At RH < 20%, the wear rate was very low even though the dissipated energy was relatively high. On the basis of the analysis in section 3.1, the nanowear of Si/SiO₂ was not dominated by the RH dependence of capillary force. At this low RH condition, the tribochemical reaction may not occur readily because the amount of the adsorbed water at the interface would be very low; so the dissipation of frictional energy may occur mostly through the lattice vibration of the sliding solid materials.

In summary, the relative humidity drastically affected the friction force of the Si/SiO₂ interface. During the wear process, the low and constant friction force usually resulted in negligible wear. In contrast, a large variation of friction force was normally accompanied by serious wear of silicon. The AFM wear test results suggested that the silicon-based MEMS might be less susceptible to wear if operated in dry air or high humidity environments.

4. DISCUSSION

4.1. Tribochemical Wear of Si/SiO₂ Interface in Humid Air. It was reported that tribochemical wear would occur on the silicon surface when there is a sufficient amount of water in the environment.¹⁰ The native oxide on a silicon surface is known to have a high concentration of hydroxyl groups.^{23–25} The dehydration and condensation reaction between Si—OH groups can occur at tribological interfaces:^{19,20,24,26}



If this reaction occurred between vicinal silanol groups on one surface, then the wear track would become hydrophobic.²¹ When this reaction occurs between two hydroxyl groups from the opposite solid surfaces, then it would result in the formation of the Si—O—Si bridges across the sliding interface, as shown in Figure 6.^{10,19,20} As both solid surfaces are compressed and

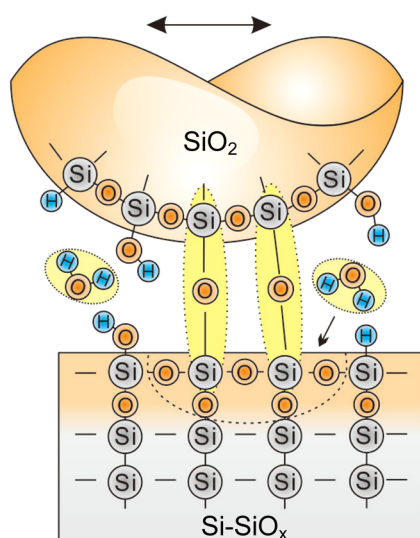
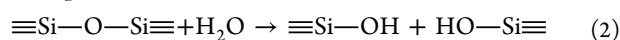


Figure 6. Illustration showing the tribochemical wear on the silicon surface.

sheared, the Si—O—Si networks in the contact area would be strained.^{19,20} The strain could facilitate the hydrolysis reaction of H₂O with the Si—O—Si network by reducing the activation energy necessary to break the Si—O bond, as shown in Figure 6 and eq 2.^{19,20,27}



If the hydrolysis of the surface Si—O—Si network continues, then the surface Si atom can be removed as Si(OH)₄. After the native oxide layer of the silicon surface is worn off, the Si—Si

backbonds of the silicon surface could also be hydrolyzed by reactions with H₂O.^{18–20} Then, the tribochemical wear of silicon will then continuously occur by the reciprocating motion of the SiO₂ tip.

The wear of silicon is dominant by mechanical removal when the contact pressure is larger than the critical contact pressure of silicon (11.3 GPa).^{28,29} In this case, amorphization or distortion of the crystalline lattice occurs beneath the wear area of silicon.^{28,29} However, when the contact pressure was much smaller than the critical contact pressure of silicon, the silicon wear would be mostly via tribochemical reactions, rather than mechanical processes.¹⁰ The tribochemical reactions would involve only the atoms at the outermost surface of the silicon substrate, and the subsurface of silicon would be intact.^{10,30,31} Therefore, if the wear of silicon were dominated by the tribochemical process, then no destruction of the silicon crystalline lattice would be observed beneath the wear area of silicon.

To confirm the tribochemical origin of the wear process in humid conditions, the cross-sectional TEM analysis was used to find any structural deformation beneath the silicon wear area. The wear track for the TEM analysis was created using the same SiO₂ AFM tip at ~50% RH. To produce a ~10 nm deep groove on the silicon surface, as shown in Figure 7(a). The TEM image in Figure 7(b) showed the cross section of the scratch. The high resolution TEM images in Figure 7(c) and (d) indicated that the silicon crystal lattice beneath the wear track is not distorted at all. This result suggested that the serious wear on silicon surface cannot be attributed to the mechanical interaction; it must be due to the tribochemical reaction.

In a previous study, the chemical species in the wear scars on the silicon substrate were analyzed with X-ray photoelectron spectroscopy (XPS) and time-of-flight secondary ion mass spectrometry (ToF-SIMS).^{32,33} The XPS analysis result confirmed the presence of oxide layers in the wear track and the occurrence of oxide reaction in the wear process.³² Furthermore, the intensities of the SiOH⁺ and SiH⁺ groups detected by ToF-SIMS were higher in the wear debris region, compared to the original silicon surface.³³ These results

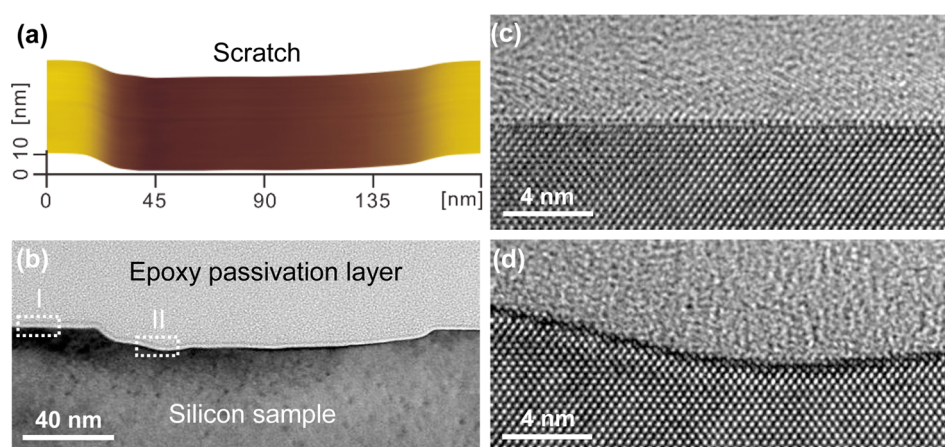


Figure 7. TEM observation on the cross section of a scratch on silicon surface caused by tribochemical wear of SiO₂ tip in humid air. (a) AFM image showing the three dimensional topography of the scratch on silicon surface; (b) TEM image showing the cross section of the scratch; (c) HRTEM image of the original area taken from the white frame I in (b); (d) HRTEM image of the worn area taken from the white frame II in (b). Because the amorphous oxide layer revealed a featureless microstructure similar to that of the passivation layer used in the sample preparation, it was difficult to identify the amorphous oxide layer inside the wear track in TEM images.

supported that tribochemical reactions at the Si/SiO₂ interface occur during the sliding process in humid air.

4.2. Suppression of Tribochemical Wear at High RHs.

The wear of silicon decreased as RH was increased from 50% to 80% and finally became negligible when the RH was above 85%. This is in drastic contrast to the large increase of wear when the RH was changed from 10% to 50%.

In the mechanism schematically illustrated in Figure 6, the prerequisite for tribochemical wear to occur is the formation of the Si_{tip}—O—Si_{substrate} bonding bridges. The formation of Si_{tip}—O—Si_{substrate} bonding bridges may be affected by the structure and thickness of the adsorbed water film on two counter surfaces.^{34,35} Since it was hard to measure the actual “interfacial” water layer thickness within the contact area between the Si wafer and SiO₂ AFM tip, the water layer thickness and its structure was measured on the open surface of a clean native oxide on a silicon wafer as a function of RH.^{34,35} At RH < 10%, less than 1 monolayer of water film with a “solid-like” structure is formed on the native oxide of the silicon surface;³⁵ at RH = 10%–30%, 1–3 layers of the solid-like water film can be formed on the silicon substrate;³⁵ at RH = 30%–60%, a liquid-like water layer starts to grow on the solid-like water layer;³⁵ at RH > 60%, the liquid water layer becomes abundant.³⁵

In the low humidity regime, the solid-like water layer appears to facilitate the formation of the Si_{tip}—O—Si_{substrate} bridges across the sliding interface. Since this water layer is very thin (only a few molecules thick), it is possible for asperities to come close enough to form Si_{tip}—O—Si_{substrate} bridges across two solid surfaces. Since the sliding requires the dissociation of such bridges, the friction force is high and wear can happen readily.

As RH increases above 50%, the adsorbed water layer becomes thick and the interfacial shear will take place mostly within the liquid-like water layer region. On the basis of typical silicon oxide structures, the bond length of the “Si—O—Si” bonding bridges is expected to be around 0.324 nm,³⁶ not much larger than the thickness of a molecular water layer. As multilayers of water grow on the surface at high RH conditions, the probability for the asperities to come close enough to form Si_{tip}—O—Si_{substrate} bridges would decrease. Thus, the tribochemical reaction probability would decrease. Finally, when the thickness of adsorbed water film on the silicon surface exceeded a few nanometers at RH > 85%,³⁴ the formation of the Si_{tip}—O—Si_{substrate} bonding bridges could be almost completely suppressed.

To test the effect of water layer thickness on tribochemical wear, a control test was performed with a hydrophobic silicon wafer. The silicon wafer becomes hydrophobic after removal of the native oxide layer through etching with HF. The etched surface is terminated with Si—H, instead of SiO_x—OH. Thus, the adsorbed water layer will be much thinner on the HF-etched surface. The meniscus height of the condensed water at the substrate/tip contact region was estimated for the HF-etched surface and the native oxide surface (see Figure S6 in the SI). The calculation predicted that the water layer thickness on the hydrophobic HF-etched surface at 90% RH would be similar to that on the hydrophilic native oxide covered surface at ~75% RH. If the adsorbed water layer thickness is the main determinant of tribochemical wear, then it is expected that the HF-etched silicon wafer would wear upon rubbing with the SiO₂ AFM tip even at 90% RH. Such prediction was tested, and the result is shown in Figure 8. Indeed, the nanowear of the

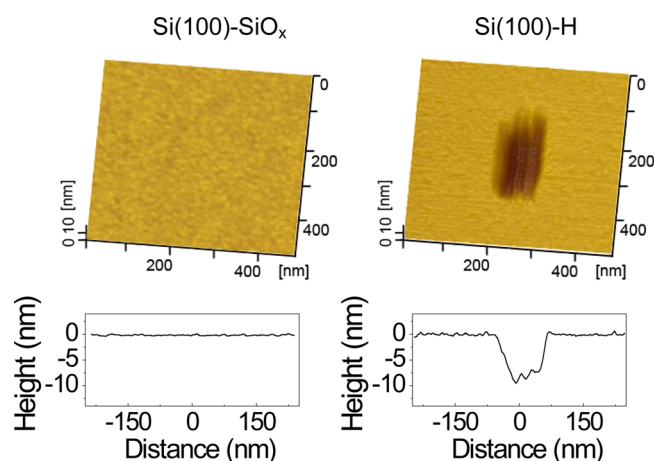


Figure 8. AFM images and cross-sectional profiles of nanowear scars on different silicon surfaces at 90% RH. $F_n = 3 \mu\text{N}$, $D = 100 \text{ nm}$, $v = 2 \mu\text{m/s}$, and $N = 200$.

hydrophobic HF-etched wafer took place at 90% RH, where the hydrophilic native oxide covered wafer did not show any discernible wear. This result confirmed that the water layer thickness, which is a function of RH as well as the substrate surface chemistry, plays an important role in tribochemical wear.

Moreover, it was reported that the isoelectric point (IEP) of silicon dioxide was around 1.7–3.5 at room temperature.³⁷ Since the pH value of DI water used in the tests was ~6.5 and the silicon sample was covered by a native oxide layer in this study, the contact interface at high RHs and in water condition would be negatively charged.^{38,39} Thus, at high RHs and underwater, the hydration layers solvating the charged surfaces could repel each other,^{38,39} minimizing direct contact or the possibility of forming the Si—O—Si bridge bonds between two solid surfaces. This might also reduce the wear of the silicon sample at high RHs and in water.

5. CONCLUSIONS

The nanowear of monocrystalline silicon was investigated for the RH range from 0% to 90% and underwater using a SiO₂ spherical AFM tip at a DMT contact pressure (1.12–1.20 GPa) and a scan speed of 2 $\mu\text{m/s}$. The humidity dependence can be divided into three regimes: low RH (<10%), low-medium RH (10–50%), and high RH (>50%). In the dry case, the mechanical damage to the silicon substrate was a hillock formation (protrusion of the surface) due to subsurface amorphization. In the low RH regime (0–10%), the hillock formation was decreased, although friction did not change substantially. As RH increased from 10% to 50%, the silicon surface wore severely via tribochemical mechanisms involving the solid-like water layers at the interface. When RH was increased further above 50%, the wear of silicon gradually decreased below the detection limit at RH > 85%. The decrease of silicon wear appeared to correlate with the formation of thick liquid-like water layer on the surface at high humidity conditions.

■ ASSOCIATED CONTENT

Supporting Information

Stability of the native oxide layer on silicon sample with the modification of the RH; effect of the adhesion force on the wear of Si/SiO₂ interface; correlation between wear volume and

wear depth of silicon; correlation between the friction force and the wear volume of silicon surface; humidity dependent friction force of the Si/SiO₂ interface; comparison of the meniscus height between Si—SiO_x/SiO₂ interface and Si—H/SiO₂ interface. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.5b03043.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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Notes

The authors declare no competing financial interest.

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