

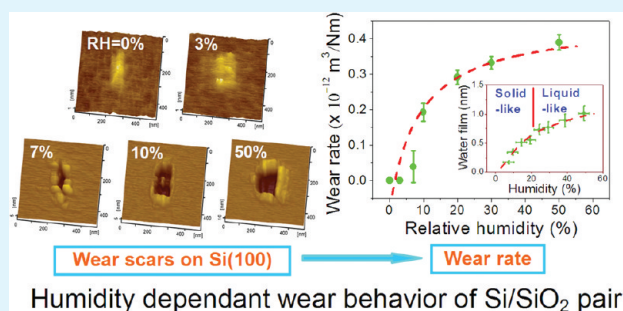
Role of Tribochemistry in Nanowear of Single-Crystalline Silicon

Jiaxin Yu,^{†,‡} Seong H. Kim,[§] Bingjun Yu,[†] Linmao Qian,^{*,†} and Zhongrong Zhou[†][†]Tribology Research Institute, National Traction Power Laboratory, Southwest Jiaotong University, Chengdu 610031, China[‡]Key Laboratory of Testing Technology for Manufacturing Process of Ministry of Education, Southwest University of Science and Technology, Mianyang 621010, China[§]Department of Chemical Engineering, The Pennsylvania State University, University Park, Pennsylvania 16802, United States

Supporting Information

ABSTRACT: The effects of counter-surface chemistry, relative humidity, and applied normal load on nanowear of single-crystalline silicon were studied with atomic force microscopy. In the absence of humidity, the silicon surface can resist mechanical wear as long as the contact pressure is lower than the hardness of silicon regardless of the counter-surface chemistry (diamond or SiO₂) and ambient gas type (vacuum, N₂, O₂, air). In these conditions, the sliding contact region is protruded forming a hillock. However, when the relative humidity is higher than ~7%, the hillock formation is completely suppressed and, instead, tribochemical wear of the silicon surface takes place even at contact pressure much lower than the hardness. The tribochemical wear increases drastically in the relative humidity regime where the adsorbed water layer assumes the “solid-like” structure; further increase of wear is small in higher relative humidity regime where the “liquid-like” water layer is formed. It is also noted that the humidity-induced wear occurs only when the counter-surface is SiO₂; but not with the diamond counter-surface. This implies that the interfacial shear of the water-adsorbed SiO₂ surface with a chemically inert counter-surface is not sufficient to initiate the tribochemical wear; both substrate and counter-surface must be chemically reactive. A phenomenological model is proposed to explain the experimental observations.

KEYWORDS: nanowear, tribochemistry, humidity, silicon, AFM,



1. INTRODUCTION

Microelectromechanical systems (MEMS) have been successfully applied in various military and commercial applications.^{1–4} In MEMS, silicon has been widely used as a structural material because of its excellent mechanical and physical behaviors as well as lithographic microfabrication techniques.^{5–7} However, tribological problems such as friction, stiction, and wear of nanoasperity silicon contacts have become a major concern in MEMS with full degrees of mechanical motions.^{5–9}

In previous single-asperity contact studies using atomic force microscopy (AFM), most of the micro/nanowear experiments on silicon were performed with diamond tips because of their excellent hardness and wear-resistance.^{10–17} Bhushan et al.^{10,11} observed that the nanowear of single-crystalline silicon by the diamond tip was due to the abrasive wear with plastic deformation. Through the in situ observation on the wear process of silicon by transmission electron microscopy (TEM), Ribeiro et al.¹² indicated that the abrasive wear was initiated by the formation and connection of dislocations along the elastic strain contour. Based on the experimental investigations and molecular dynamics simulation, Zhang et al.^{13,14} reported that deformation via amorphous phase transformation and viscous flow was an important factor inducing the silicon removal at nanoscale. The onset of amorphous transformation of silicon

surface during the sliding process could be predicted by the Von Mises stress criterion with the threshold of 4.6–7.6 GPa, depending on sliding directions.^{15,16} More recently, Yu et al.¹⁷ identified two different modes of mechanical damage of the silicon substrate: hillock (protrusion) versus groove (depression). When the critical contact pressure is lower than the hardness of silicon, the hillock formation is dominant; as the contact pressure is increased above the hardness, the plastic deformation and abrasive action create the groove.

Although the mechanical wear mechanism in the nanowear of silicon was extensively investigated, the role of tribochemistry in nanowear of crystalline silicon in humid environments is far less understood.^{10–17} In fact, the nanowear of the Si/Si pair or Si/SiO₂ pair should be the essential issue in the dynamic MEMS devices. For example, when the nanowear tests were performed by a side-wall friction MEMS in ambient air, large amorphous debris particles with high oxygen content were observed after a short-time operation, which indicated that serious tribochemical reactions occurred in the MEMS.¹⁸ On the basis of the experimental results obtained with ball-on-disk

Received: December 12, 2011

Accepted: February 20, 2012

Published: February 21, 2012



tester in air and nitrogen, Mizuhara et al.¹⁹ emphasized the role of tribochemical reaction in the wear process of the Si/SiO₂ pair. From the nanowear tests with AFM, Yu et al.²⁰ found that the nanowear of the Si/SiO₂ pair was more severe on hydrophilic surfaces than hydrophobically treated surfaces. Compared with the mechanical interaction, the tribochemical reaction played a dominant role in the nanowear of the Si/SiO₂ pair in humid conditions. Recently, Barnette et al.²¹ demonstrated the protection of the Si/SiO₂ pair from wear damage in alcohol vapor environments. Despite all these studies, the quantitative understanding on the transition from the mechanical to tribochemical wear behaviors or their contributions to the total wear of single-crystalline silicon has not been well-addressed.

In this paper, the nanowear of single-crystalline silicon was systematically studied with AFM as functions of ambient gas composition, surface chemistry of the sliding counterface and applied normal load. The tribochemical reaction inducing nanowear of the Si/SiO₂ pair was found to depend on not only water adsorption but also reactive counter-surface chemistry. This provides further insights into the reaction mechanism involved in tribochemical nanowear of Si/SiO₂ interfaces.

2. MATERIAL AND METHODS

The p-doped Si(100) wafers with a thickness of 0.5 mm were purchased from MEMC Electronic Materials, Inc., USA. With an AFM (SPI3800N, Seiko, Japan), the root-mean-square (rms) roughness of the silicon wafer was measured as 0.07 nm over a 500 nm × 500 nm area. The native oxide layer on silicon surface was measured to be about 0.5 nm by a scanning Auger nanoprobe. The static water contact angle was ~39°, implying that the surface is partially hydrophilic.^{22,23}

All nanowear tests and in situ topography scanning were carried out with the AFM equipped with an environment chamber with a vacuum capability. Two kinds of tips were used for nanowear tests: SiO₂

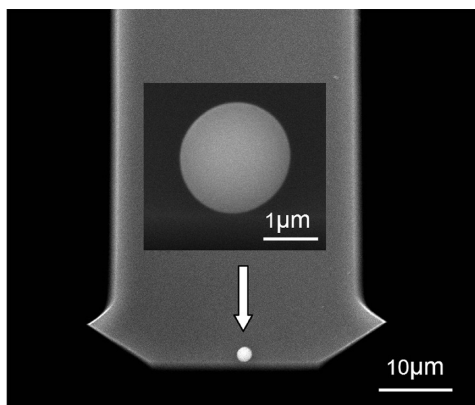


Figure 1. SEM image of SiO₂ tip using in nanowear tests. A SiO₂ microsphere was glued on a cantilever of AFM probe, and the radius of the SiO₂ microsphere was about 1.0 μm.

microsphere and diamond spherical tip. As shown in Figure 1, the SiO₂ microsphere was glued on a cantilever of AFM probe (Novascan Technologies, USA). The radii of the SiO₂ microspheres were about 1.0 μm. The normal spring constants of the cantilevers were calibrated using a standard calibration cantilever and found to be in the range of 16.8–19.7 N/m.²⁴ The SiO₂ microsphere probes were used as purchased. The diamond tip has a radius of 0.3 μm. The spring constant of its cantilever was ~203 N/m. The nanowear tests were performed through a single-line reciprocating sliding mode.^{17,20} To record the friction force, the tip was scanned along the lateral direction to the cantilever. The sliding displacement amplitude *D* was 100 nm if

not specifically mentioned, and the number of nanowear cycles *N* was 200 or 500. The applied load *F_n* was varied between 1 to 10 μN. The friction force of the tests was calibrated by a modified wedge method using a silicon grating with a wedge angle of 54°44' (TGF11, MikroMasch, Germany).^{25,26} After nanowear tests, the topography of the wear area was scanned with a sharp silicon nitride tip, which has a nominal tip curvature radius of 20 nm and a nominal spring constant of 0.1 N/m (MLCT, Veeco, USA). The scan size of the AFM images was 500 nm × 500 nm.

Four different atmosphere conditions were used for nanowear tests: vacuum (<5.0 × 10⁻⁶ Torr), nitrogen, oxygen, and dry air (water vapor is less than 0.005%). The ambient pressure for nitrogen, oxygen, and dry air were 1200 Torr. The effect of relative humidity (RH) on nanowear was studied in the RH range between 0 and 50%. To avoid any uncertainty due to tip shape changes, we used a new SiO₂ tip for each nanowear experiment. During the tests, the friction and adhesion behavior of the tips were carefully calibrated.²⁷ For instance, the humidity dependent nanowear experiments were successively performed with a single SiO₂ tip at RH 0, 3, 7, 10, 20, 30, and 50%, and then repeated at RH 0%. Only when the measurements of the friction, adhesion, and nanowear of the Si/SiO₂ pair at 0% RH were reproduced were the humidity data considered to be valid. Otherwise, the tip was replaced and the same procedure was repeated.

3. EXPERIMENTAL RESULTS

3.1. Resistance of Silicon Surface to Mechanical Wear in Inert Conditions.

Figure 2a shows the AFM images of silicon surfaces scratched under vacuum, pure nitrogen, pure oxygen and dry air conditions. After 200 cycles of wear tests under a normal load of 5 μN, the surface damage was identified as hillocks (less than 1 nm tall). The formation of hillock on silicon surface is distinct from typical wear which normally means material removal.^{28,29} Previous studies revealed that the hillock was formed within a few scratching cycles under the given conditions and then grew as the rubbing cycle increased.¹⁷ Through TEM analyses, it was found that these hillocks were accompanied by subsurface deformation to amorphous structures caused by mechanical interaction.^{30,31}

During the scratch test, the friction force *F_t* was recorded as a function of wear cycle *N* (*F_t* - *N* curves), as shown in Figure 2b. When the hillocks were generated on the silicon surface, the friction force *F_t* of the Si/SiO₂ pair was relatively stable over the duration of the entire nanowear test cycle. The *F_t* in vacuum presented the lowest value.²⁰ The *F_t* values in pure nitrogen, pure oxygen, and dry air were slightly higher than that in vacuum. This could be due to a trace amount of water vapor in the ambient dry conditions. Because the ambient pressure was 1200 Torr and the water vapor content was less than 0.005% in all three ambient conditions, the water vapor pressure could be as high as 0.06 Torr, which corresponded to RH < 0.25%. The slight decrease of the friction force with the rubbing cycle in vacuum was not fully understood; but it might be speculated that the hillock formation on the substrate surface could reduce the effective contact area with the tip.

3.2. Transition from Mechanical Deformation to Tribochemical Wear.

The transition from mechanical deformation to tribochemical wear of the Si/SiO₂ pair was investigated in air at various RH. Figure 3a shows the AFM images of wear scars on silicon. When RH was 0 or 3%, the mechanical deformation was the main surface damage and the friction scars presented hillocks. However, when RH was equal to or higher than 7%, all wear scars appeared as grooves under the same loading conditions. This suggests that the surface damage of silicon is changed from mechanical deformation to tribochemical wear. Because the water adsorption will not alter

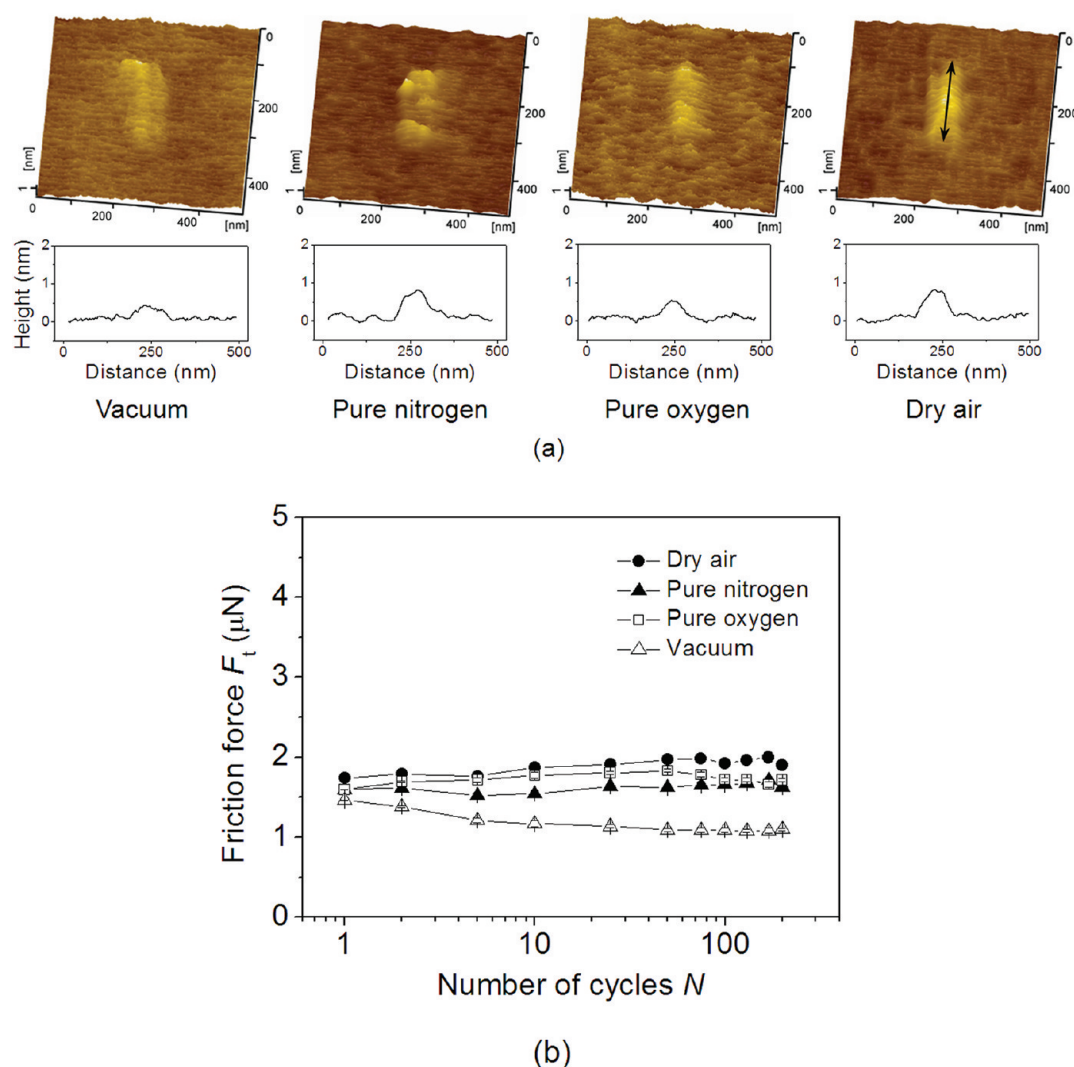


Figure 2. Effect of ambience on the wear of silicon against SiO_2 tip. (a) The AFM images and cross-sectional profiles of wear scars on silicon surface obtained in various ambiances under $F_n = 5 \mu\text{N}$. A line was inserted into figure to show the scratch direction of the tip. (b) The friction force F_t versus the number of wear cycle N (F_t - N) curves of silicon against SiO_2 tip in various ambiances.

the subsurface mechanical properties, the observed humidity effect is more likely due to the tribochemical surface reactions, than the subsurface fatigue or crack formation.

The groove depth (or wear volume) appeared to correlate with the thickness and structure of water film adsorbed on the silicon surface (Figure 3b).³² Here, the thickness of water film used in Figure 3b was taken from the previous study by Asay et al.^{32–34} It is extremely difficult to measure the adsorption isotherm of water on the wear track during the subsequent sliding cycles. However, the water adsorption on the worn surface is expected to readily take place, since the partial pressure of water vapor is high (>1 Torr) and the slide interval (about 0.25 s) is much longer than the time required forming one monolayer at these pressure conditions. In the RH regime below 20%, the adsorbed water layer assumes a “solid-like” structure.^{32,33} As the RH increases in this regime, the wear depth increased sharply from 0.8 nm protrusion (hillock) to 10.0 nm depression. With the further increase in RH above 20%, the wear depth increased slowly and leveled off at ~ 11 nm. At $\text{RH} \geq 20\%$, a liquid structure starts to grow on the solid-like structure in the adsorbed water layer.^{32–34} These results imply that the structure of water could be one of the

hypotheses to explain the observed RH dependence of the tribochemical wear. The wear appears to be severe when the adsorbed water layer behaves like a solid and the fluid-like water layer does not seem to play an important role in the wear of silicon.³³

The corresponding F_t - N curves were shown in Figure 3c. It is found that the initial friction force reveals an increase with relative humidity, which is due to the meniscus formation on the contact area of Si/ SiO_2 pair.³⁵ Because of the negligible wear of silicon surface at 0 and 3% RH, F_t was relatively constant over the duration of wear test. However, when the RH was above 7%, F_t initially increased to a maximum value and then decreased to a low-friction value. The initial increase of friction might be attributed to the increase in the real contact area caused by initial wear from the flat surface to a grooved shape. Although it is not fully understood yet, one can speculate that the reason for the subsequent decrease of friction force is due to the third-body contact interactions of trapped wear particles at the sliding interface and the change of interface between the SiO_2 tip and the native oxide surface to the SiO_2 tip and the worn Si surface.^{20,36} During the wear process, the wear particles may adhere to the SiO_2 tip surface. As a result,

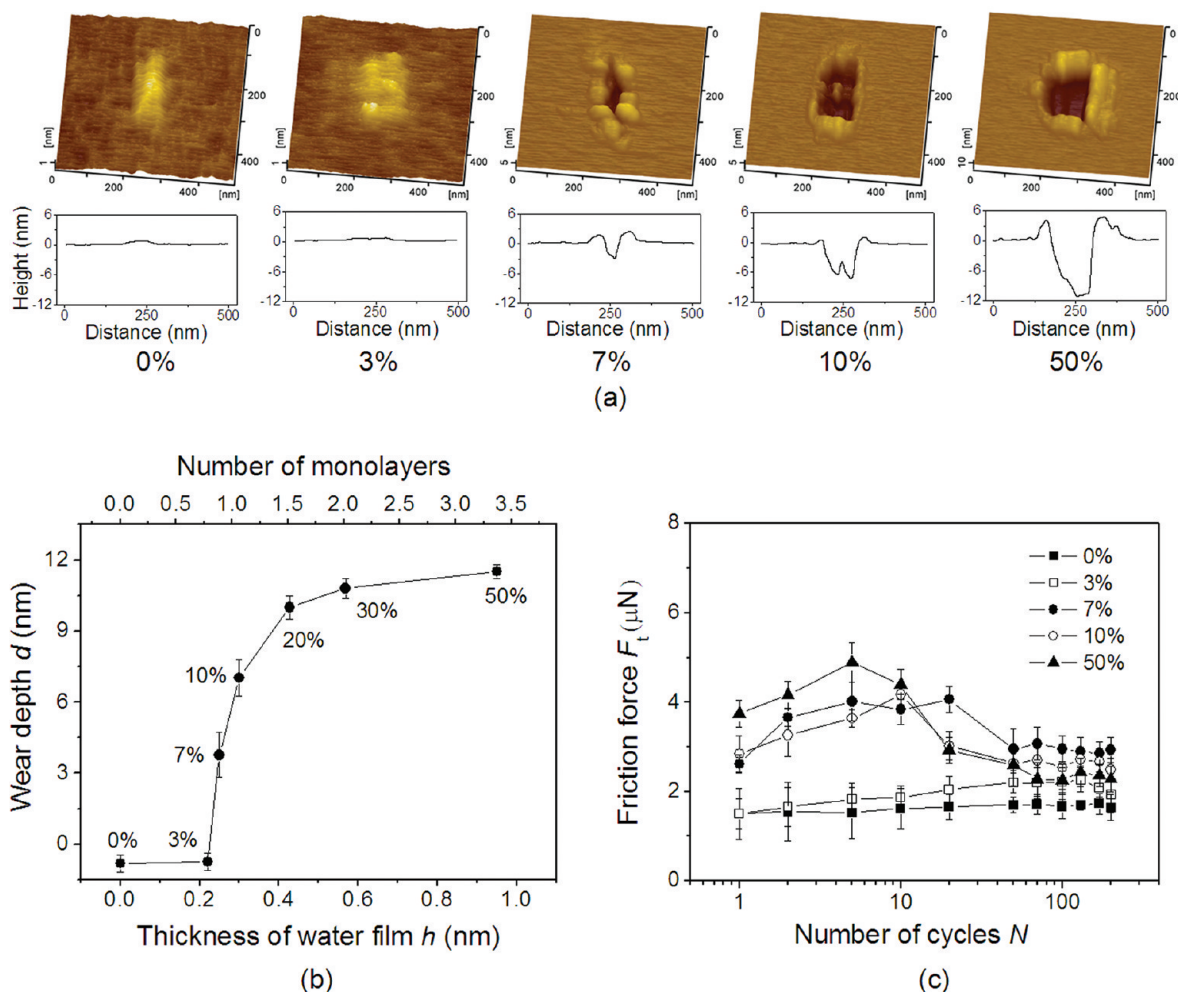


Figure 3. Effect of relative humidity of air on the wear of silicon against SiO_2 tip. (a) The AFM images and cross-sectional profiles of wear scars on silicon surface obtained in air with various relative humidity under $F_n = 5 \mu\text{N}$. (b) The variation of wear depth of the scars in Figure 3a with the film thickness of the adsorbed water molecules on silicon substrate. (c) The F_t - N curves of silicon against SiO_2 tip in air with various relative humidity.

the actual contact area may decrease. This will cause a decrease in adhesion. The decrease in the adhesive contribution to the total load can be manifested as a lower friction (see the Supporting Information).³⁷

Not only the adsorbed water layer but the chemistry of the counter-surface is also important in the transition from mechanical deformation to tribochemical wear of silicon. The wear behavior of silicon surface was tested with a diamond tip in vacuum and in humid air of RH = 35% and compared with the wear behavior observed with the SiO_2 tip. Figure 4a shows the AFM images of wear scars on silicon obtained with the diamond tip. When the wear tests were performed in vacuum, the wear scars generated by the diamond tip presented hillocks, which was similar to the wear scars generated by the SiO_2 tip in vacuum (Figure 2a). However, when the wear tests were performed with the diamond tip in humid air, no groove was found on the silicon surface under a load of $5 \mu\text{N}$. Even if the load was increased to $10 \mu\text{N}$, the friction scar still presented hillock. These results were quite different from those obtained with the SiO_2 tip, where an 11 nm deep groove was generated in humid air under a load of $5 \mu\text{N}$, as shown in Figure 4b.

The above results suggest that with the humidity alone, the tribochemical wear of the substrate is not guaranteed; the counter-surface chemistry is an important parameter for the

wear process of the single-crystalline Si surface. Figure 4c shows the comparison of the F_t - N curves obtained with the diamond and SiO_2 tips. It was found that when the hillocks were generated during the wear process, the F_t of the Si/diamond pair remained unchanged with the increase in N both in vacuum and humid air. However, when the serious wear (material removal) occurred in humid air, the F_t of the Si/ SiO_2 pair revealed a large variation.

The mechanical wear of silicon surface is strongly dependent on the contact pressure.^{10,11} To understand the effect of contact pressure on the tribochemical wear of the Si/ SiO_2 pair, the wear tests were performed under various applied loads F_n in humid air of RH = 35%. As shown in Figure 5a, with the increase of F_n from 1 to $5 \mu\text{N}$, the corresponding DMT contact pressure increases from 0.94 to 1.38 GPa and the depth of wear scars increases from 4.4 to 10.5 nm. The results indicate that the increase of the contact pressure can significantly enhance the tribochemical wear of the Si/ SiO_2 pair. It should be noted that the DMT contact pressure tested in this experiment was much smaller than the silicon hardness. Thus, the wear of silicon surface may be mainly due to tribochemical reactions, rather than mechanical actions. Figure 5b shows the F_t - N curves of the Si/ SiO_2 pair under various normal loads. In all cases, the friction force F_t varies similarly with the increase of N .

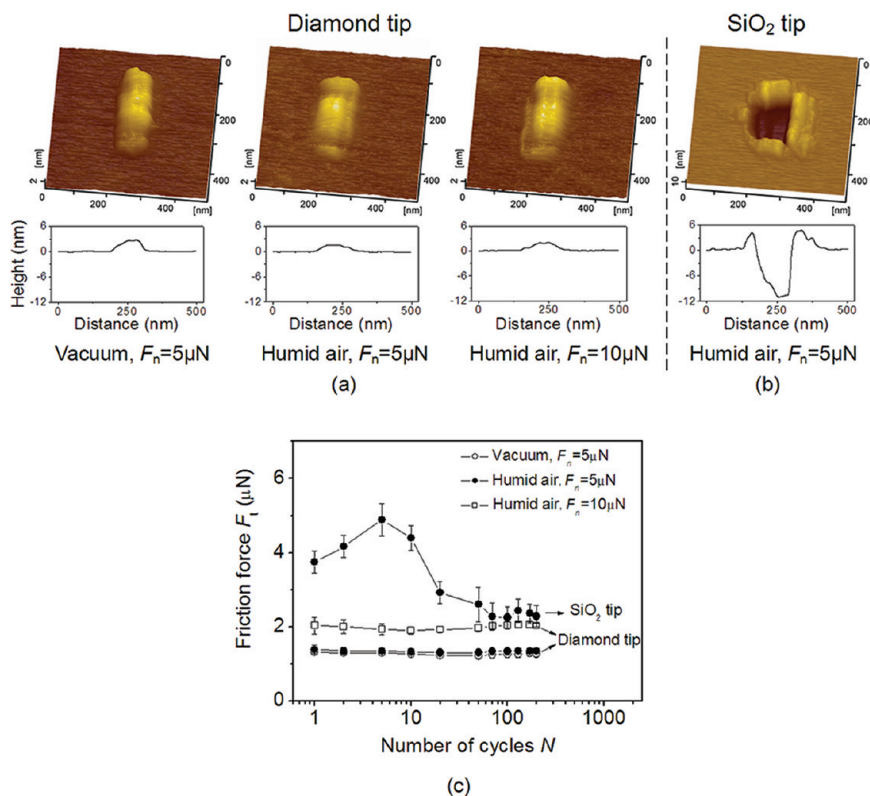


Figure 4. Comparison of the wear of Si/diamond pair and Si/SiO₂ pair. (a) The AFM images and cross-sectional profiles of wear scars on silicon surface worn by diamond tip in vacuum and humid air. (b) The AFM images and cross-sectional profiles of wear scars on silicon surface worn by SiO₂ tip in humid air. (c) The F_t - N curves of silicon against diamond tip and SiO₂ tip in vacuum and humid air.

4. DISCUSSIONS

4.1. Role of Tribochemical Reaction in the Nanowear of Si/SiO₂ Pair. The severe wear of the Si/SiO₂ pair in humid environments may be mainly due to the consequence of chemical reactions induced or facilitated by mechanical stress (see the Supporting Information). In the present experiment, the maximum DMT contact pressure P_c can be estimated by³⁸

$$P_c = \frac{3}{2\pi} \left[\frac{K^2}{R^2} (F_n + F_a) \right]^{1/3} \quad (1)$$

where the combined elastic modulus $K = 64.8$ GPa and the tip radius $R = 1$ μm . With the normal load $F_n = 5$ μN and the adhesion force $F_a = 0.8$ μN at the humidity of 35%, the maximum contact pressure P_c is calculated to be 1.38 GPa. The critical contact pressure P_y for the initial yield of silicon can be estimated in the following. Because the Poisson ratio of silicon is 0.28,⁹ the principal shear stress τ_c is calculated by³⁹

$$\tau_c = 0.31P_c \quad (2)$$

The critical contact pressure P_y for plastic deformation can be estimated from the Tresca yield criterion $(\tau_c)_{\max} \leq 0.5\sigma_y$

$$P_y = \frac{1}{0.31} (\tau_c)_{\max} = \frac{1}{0.31} 0.5\sigma_y = 1.61\sigma_y \quad (3)$$

Because the yield stress σ_y of Si(100) is 7 GPa,⁴⁰ the critical contact pressure P_y can then be estimated from eq 3 as 11.3 GPa, which is close to the hardness of Si(100) (11–13 GPa).^{41,42} In the wear tests of Si/SiO₂ pair, since the maximum contact pressure P_c (1.38 GPa) was much lower than the critical contact pressure P_y (11.3 GPa), the contact between silicon and

the SiO₂ tip must be elastic. This implies that the mechanical interaction will not induce the plastic deformation of silicon surface under the given loading conditions. Therefore, the deep scratch groove on the silicon surface created by rubbing with the SiO₂ counter-surface in humid air must be due to chemical reactions induced or facilitated by mechanical shear. Note that without shear, there is no wear of the substrate (see the Supporting Information). It was suggested that the chemical reaction can reduce the threshold stress inducing wear of mica in humid air.^{43,44}

4.2. Role of Water Molecule in the Tribochemical Reaction of Si/SiO₂ Pair. Water vapor plays a critical role in the nanowear of the Si/SiO₂ pair, as shown in Figures 2 and 3. The data show the quantitative relationship between the wear rate and the amount of adsorbed water. As shown in Figure 6, the wear rate of silicon surface increases sharply from 3% RH to 20% RH and then becomes relatively stable at RH > 20%. Here, the wear rate was determined by dividing wear volume by friction work. Such a trend can be compared with the thickness and structure of the adsorbed water layer on silicon surface. The inset picture in Figure 6 shows the adsorption isotherm of silicon surface in humid air reported by Asay et al.^{32,33} When the RH is above $\sim 20\%$, the adsorbed water film is more than three layers and the liquid-like structure grows on the solid-like structure. It is interesting to see that the wear increases significantly in the region where the adsorbed water layer structure is solid-like (ice-like), and it increases slowly in the RH region where liquid-like water structure is formed.^{32–34} In other words, when the adsorbed water layer is thin and hydrogen strongly bonded to the substrate surface with little fluidicity, the contribution of water molecules to wear is large.

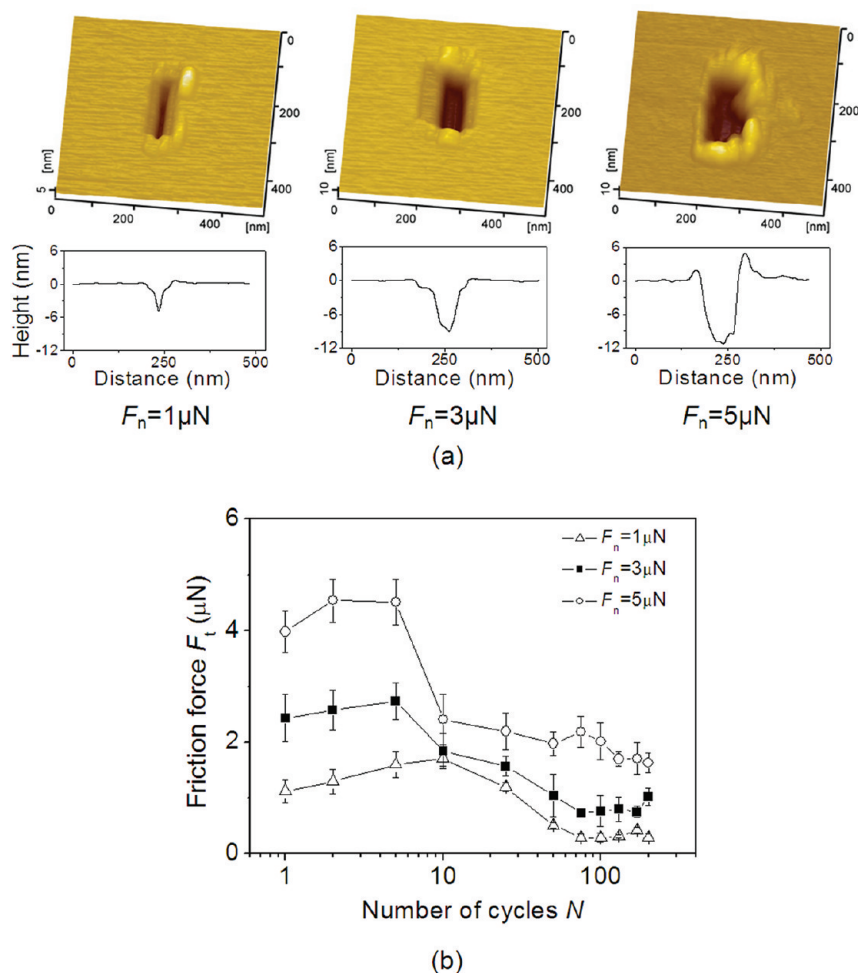


Figure 5. Effect of applied normal load on the wear of silicon against SiO_2 tip in humid air with 35% RH. (a) The AFM images and cross-sectional profiles of wear scars on silicon surface at various normal loads in humid air. (b) The F_t - N curves of silicon against SiO_2 tip at various normal loads in humid air.

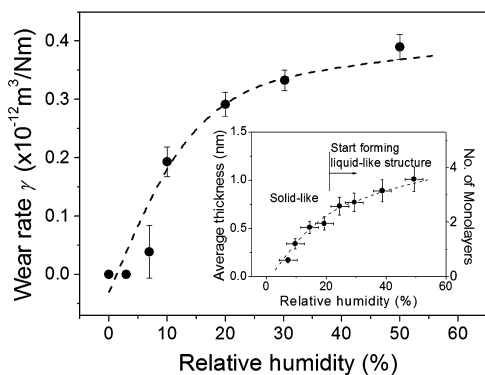


Figure 6. Dependence of the wear rate of Si/ SiO_2 pair on the quantity of water molecules adsorbed on the silicon surface. The inset picture shows the adsorption isotherm of $\text{SiO}_2/\text{Si}(100)$ surface in humid air reported previously.^{31,32}

When the adsorbed water layer is thick enough to behave like a fluid, i.e., water molecules readily form and break hydrogen bonds with neighboring molecules, then their contribution to the substrate wear is small. This fact could be used to support the tribochemical mechanism of silicon surface in water.^{45–48}

4.3. Role of Counter-Surface Chemistry in the Nano-wear of Silicon. Another important finding of this study is

that the water adsorption alone is only a necessary condition, but not a sufficient condition for tribochemical wear. If the sliding counter-surface is not reactive enough, then tribochemical reaction does not occur. Figure 4 shows the friction scar when the diamond tip was used and the maximum contact pressure P_c was 4.8 GPa under $F_n = 10 \mu\text{N}$. Because P_c was lower than the critical contact pressure P_y (11.3 GPa), no plough was observed. This contact pressure is about 5 times higher than the lowest contact pressure tested with the SiO_2 tip ($1 \mu\text{N}$; Figure 5); but there is still no tribochemical wear. This indicates that the tribochemical reaction occurring at the Si/ $\text{H}_2\text{O}/\text{SiO}_2$ interface does not take place at the Si/ $\text{H}_2\text{O}/$ diamond interface even at much higher contact and shear stress. Compared with the diamond tip, the SiO_2 tip more readily induces the tribochemical reaction of the silicon surface during the wear process. Scanning X-ray photoelectron spectroscopy (XPS) detection suggested oxidation of the silicon surface in the wear region (see the Supporting Information).

The data presented here support the reaction mechanism proposed for tribochemical wear of Si/ SiO_2 pair, as shown in Figure 7.^{45–47} It was previously thought that during the wear process, the water molecules can rupture the Si–Si and Si–O bonds on silicon substrate through the hydrolysis reaction.^{45,48} According to the mechanism of water-induced corrosion of

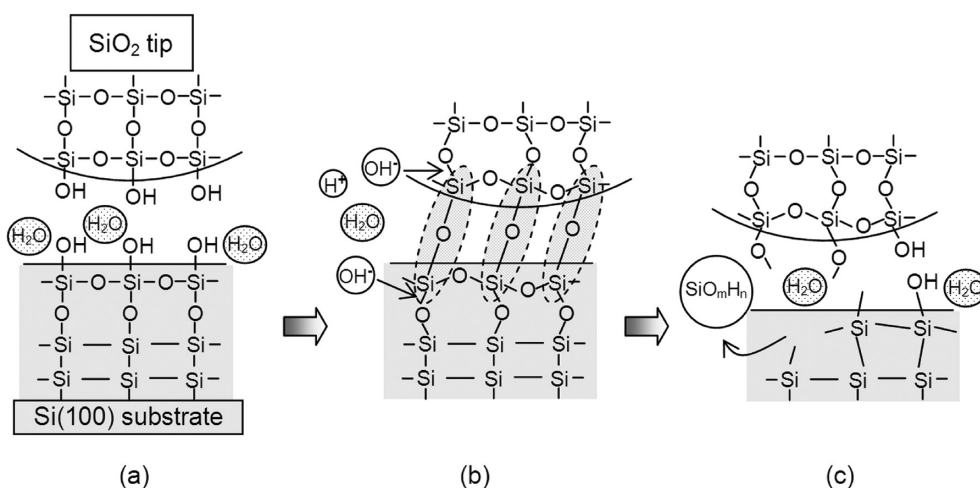
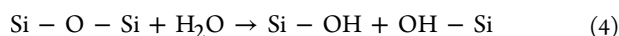
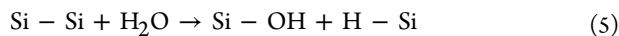


Figure 7. Schematic of the possible tribochemical reaction process of Si/SiO₂ pair. (a) The initial state of Si/SiO₂ pair before wear. (b) The formation of tip–substrate bridges facilitating the attack of water molecules. (c) The occurrence of wear with the departing of tip–substrate bridges.

silica, water can hydrolyze and dissociate the Si–O–Si network on the native oxide layer of silicon and on the SiO₂ tip.^{45,48}



After the native oxide layer of silicon were removed, the Si–Si network of silicon substrate can also be decomposed by water¹⁹



The hydrolysis of the Si–O–Si and Si–Si networks produces silane compounds, which can be desorbed or removed during or after the shear action of the interface.

Our results suggest that the water-induced interfacial reactions at silicon or SiO₂ surface can lead to wear only when the adsorbed water layer has the solid-like structure bridging both sliding surfaces (Figure 7). With the help of water molecules, the SiO₂ tip can be chemically associated to the silicon substrate forming Si–O–Si bridges (Figure 7b).⁴⁷ During sliding, the interfacial Si–O–Si bridges would be strained or stretched and the energy was stored in the stretched bridging bonds. Such a strained Si–O–Si network might be more susceptible for the hydrolysis reaction leading to the removal of Si(OH)₄. After mechanical shearing, some Si–O– and Si– dangling bonds will be exposed at the surface of SiO₂ tip and silicon surface (Figure 7c).^{45,46} The Si– dangling bond on silicon can easily link the Si–O– groups on SiO₂ tip to form a new Si–O–Si bridge between the silicon substrate and SiO₂ tip. The formation of the interfacial Si–O–Si bridges can effectively relay the subsequent mechanical shearing stress to the substrate and tip surfaces and facilitate a further attack by H₂O molecules.

In this tribochemical mechanism described here, the absence of tribochemical wear in the diamond tip sliding could be explained by the following two factors. First, the diamond surface may not readily form the interfacial bridge like the Si–O–Si bond. Second, the structure of the water layer on the diamond surface may be more fluidic than that on the SiO₂ surface. Without the covalent bridge or the solid-like water layer, the tribochemical wear of the silicon surface does not take place readily.

Recently, Barnette et al.²¹ reported that the adsorption of water molecules facilitates wear of the Si/SiO₂ interface. In contrast, the adsorption of n-pentanol molecules prevents wear of the SiO₂ surface. Based on the density functional theory

(DFT) calculations, they explained that the alkoxide termination of the SiO₂ surfaces increased the energy barrier required to cleave the Si–O–Si bonds when compared to the hydroxyl-terminated SiO₂ surface. In our experiments, we found that the mechanical shear of the water-adsorbed SiO₂ surface with chemically inert counter-surface is not sufficient; both the substrate and the counter-surface must be chemically reactive. The mechanism described in this paper can also explain the wear prevention effect of the alcohol covered surface. Unlike the silanol group, the alkoxide group at the SiO₂ surface is difficult to form the bridge with the SiO₂ counter-surface.

The wear tests of the Si/SiO₂ pair in vacuum (Figure 2a) or the Si/diamond pair in vacuum and in air (Figure 4a) revealed that the mechanical interaction can cause only a mild mechanical damage (hillock formation) on silicon under the given loading conditions. However, once the water molecules and the reactive counterface are involved, the consequence of the same mechanical interaction becomes very different. The mechanical interaction (compression and shear) are needed to dissociate the Si–O–Si covalent bond. In most cases, rates of bond breakages are greatly enhanced by the synergistic action of mechanical and chemical stimuli.⁴⁴ The DFT calculations found that the activation energy for this reaction is larger than 100 kJ/mol.²¹ Since thermal energy available at room temperature is only ~2.5 kJ/mol (8.3 J/(mol K) × 300 K), this reaction cannot occur at room temperature. One may speculate the frictional heating at the asperity contact; but since the sliding speed was low (0.8 μm/sec) and the thermal conductivity of silicon is high (149 W/(mol K)), the frictional temperature increase was calculated to be only 22 K, which is not sufficient to overcome the >100 kJ/mol activation energy.⁴⁹ Thus, there must be a mechanism transferring some of the interfacial shear force or energy to the dissociation process of the Si–O–Si bridge bond. It was accepted that the water molecules can react directly with the strained Si–O bond because of the ability of water to donate both electrons and protons to the strained bond.^{50,51} Molecular dynamics simulations indicated that the activation barrier of hydrolysis reaction decreased in proportion to the applied stress.⁵⁰ With the increase in the applied shear stress, the hydrolysis of the Si–O–Si network leading to the material removal becomes more facile.⁵⁰

5. CONCLUSIONS

The effects of ambient humidity, surface chemistry of the friction counterface, and applied load on the tribochemical reaction of the Si/SiO₂ pair were addressed. Both water adsorption and reactive counter-surface chemistry were found to be the necessary conditions for the tribochemical reaction inducing nanowear of Si/SiO₂ pair. The main conclusions can be summarized as follows. First, in the absence of water vapor, the silicon surface can largely resist mechanical wear as long as the contact pressure is lower than the hardness of silicon regardless of the counter-surface chemistry (diamond or SiO₂) and ambient gas type (vacuum, N₂, O₂, dry air). In these conditions, the surface deformation results in hillocks, rather than material loss. Second, with the increase in the RH of humid air, the damage of Si/SiO₂ pair will transform from mechanical deformation (protrusion) to tribochemical wear (material loss) under the sliding velocity of 0.8 μm/s and the contact pressure of 1.38 GPa. The tribochemical wear volume increases in the RH regime (<20%) where the adsorbed water layer forms the solid-like structure; once RH is increased above 20% and the adsorbed water layer forms the liquid-like structure, the further increase of tribochemical wear is insignificant. Third, the surface chemistry of the friction counterface is an important factor to initiate the tribochemical wear of Si/SiO₂ pair. If the sliding counter-surface is not reactive enough, then tribochemical reaction does not occur. Finally, mechanical interaction is not a dominant factor, but a necessary constituent for tribochemical wear. Without mechanical compression and shear by the reactive counterface, tribochemical wear of the Si surface does not take place readily.

■ ASSOCIATED CONTENT

Supporting Information

Comparison of the wear of Si/SiO₂ pair in vacuum and in humid air; variation of the friction of Si/SiO₂ pair with the wear cycles in humid air; effect of shear stress on the wear of Si/SiO₂ pair; detection of chemical contents on the wear scars by scanning X-ray photoelectron spectroscopy (XPS). This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: linmao@swjtu.edu.cn. Tel.: +86 28 87600687. Fax: +86 28 87603142.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors are grateful for the financial support from supported by National Basic Research Program (2011CB707604) and Natural Science Foundation of China (51175441, 90923017). S.H.K. was supported by the National Science Foundation (Grant CMMI-100021).

■ REFERENCES

- (1) Cui, Z. *Micro-nanofabrication Technologies and Application*; Higher Education Press: Beijing, 2005.
- (2) Elwenspoek, M.; Wiegerink, R. *Mechanical Microsensors*; Springer: Berlin, 2001.
- (3) Tanaka, M. *Microelectron. Eng.* **2007**, *84*, 1341–1344.
- (4) Ko, W. H. *Sens. Actuators, A* **2007**, *136*, 62–67.

- (5) Bhushan, B. *Modern Tribology Handbook*; CRC Press: Boca Raton, FL, 2001; Vol. 1.
- (6) Williams, J. A.; Le, H. R. *J. Phys. D* **2006**, *39*, R201–R214.
- (7) Kaneko, R.; Umemura, S.; Hirana, M.; Andoh, Y.; Miyamoto, T.; Fukui, S. *Wear* **1996**, *200*, 296–304.
- (8) Hsu, W. C. U.S. Patent 6 200 207.
- (9) Tanaka, H.; Shimada, S. *Ann. CIRP* **2007**, *56* (1), 53–56.
- (10) Bhushan, B.; Israelachvili, J. N.; Landman, U. *Nature* **1995**, *374*, 607–616.
- (11) Zhao, X.; Bhushan, B. *Wear* **1998**, *223*, 66–78.
- (12) Ribeiro, R.; Shan, Z.; Minor, A. M.; Liang, H. *Wear* **2007**, *263*, 1556–1559.
- (13) Zhang, L.; Zarudi, I. *Int. J. Mech. Sci.* **2001**, *43*, 1985–1996.
- (14) Cheong, W. C. D.; Zhang, L. *Int. J. Mater. Prod. Technol.* **2003**, *18*, 398–407.
- (15) Zhang, L.; Tanaka, H. *Tribol. Int.* **1998**, *31* (8), 425–433.
- (16) Zarudi, I.; Zou, J.; McBride, W.; Zhang, L. *Appl. Phys. Lett.* **2004**, *85* (6), 932–934.
- (17) Yu, J. X.; Qian, L. M.; Yu, B. J.; Zhou, Z. R. *Wear* **2009**, *267*, 322–329.
- (18) Alsem, D. H.; Stach, E. A.; Dugger, M. T.; Enachescu, M.; Ritchie, R. O. *Thin Solid Films* **2007**, *515*, 3259–3266.
- (19) Mizuhara, K.; Hsu, S. M. *Tribol. Ser.* **1992**, *21*, 323–328.
- (20) Yu, J. X.; Qian, L. M.; Yu, B. J.; Zhou, Z. R. *J. Appl. Phys.* **2010**, *108*, 034314.
- (21) Barnette, A. L.; Asay, D. B.; Kim, D.; Guyer, B. D.; Lim, H.; Janik, M. J.; Kim, S. H. *Langmuir* **2009**, *25* (22), 13052–13061.
- (22) Nevshupa, R. A.; Scherge, M.; Ahmed, S. I.-U. *Surf. Sci.* **2002**, *517*, 17–28.
- (23) Opitz, A.; Ahmed, S. I.-U.; Schaefer, J. A.; Scherge, M. *Surf. Sci.* **2002**, *504*, 199–207.
- (24) Torii, A.; Sasaki, M.; Hane, K.; Okuma, S. *Meas. Sci. Technol.* **1996**, *7*, 179–184.
- (25) Varenberg, M.; Etsion, I.; Halperin, G. *Rev. Sci. Instrum.* **2003**, *74*, 3362–3367.
- (26) Yu, J. X.; Qian, L. M. *Tribology* **2007**, *27* (5), 472–476.
- (27) Qian, L. M.; Xiao, X. D. *Langmuir* **2000**, *16*, 622–670.
- (28) Kaneko, R.; Miyamoto, T.; Andoh, Y.; Hamada, E. *Thin Solid Films* **1996**, *273*, 105–111.
- (29) Yu, J. X.; Qian, L. M.; Yu, B. J.; Zhou, Z. R. *Tribol. Lett.* **2009**, *34*, 31–40.
- (30) Yu, B. J.; Dong, H. S.; Qian, L. M.; Chen, Y. F.; Yu, J. X.; Zhou, Z. R. *Nanotechnol.* **2009**, *20*, 465303.
- (31) Yu, B. J.; Dong, H. S.; Qian, L. M.; Yu, J. X.; Zhou, Z. R. *Wear* **2010**, *268*, 1095–1102.
- (32) Asay, D. B.; Kim, S. H. *J. Phys. Chem. B* **2005**, *109*, 16760–16763.
- (33) Asay, D. B.; Kim, S. H. *J. Chem. Phys.* **2006**, *124*, 174712.
- (34) Asay, D. B.; Barnette, A.; Kim, S. H. *J. Phys. Chem. C* **2009**, *113*, 2128–2133.
- (35) Syed Asif, S. A.; Wahl, K. J.; Colton, R. J. *J. Mater. Res.* **2000**, *15*, 546–553.
- (36) Liu, E.; Blanpain, B.; Celis, J.-P.; Roos, J. R. *J. Appl. Phys.* **1998**, *84*, 4859–4865.
- (37) Godet, M. *Wear* **1990**, *136*, 29–45.
- (38) Schwarz, U. D. *J. Colloid Interface Sci.* **2003**, *261*, 99–106.
- (39) Johnson, K. L. *Contact Mechanics*; Cambridge University Press: Cambridge, U.K., 1985.
- (40) Maluf, N. *An Introduction to Microelectromechanical Systems Engineering*; Artech House: Norwood, MA, 2004.
- (41) Bhushan, B. *Wear* **2001**, *251*, 1105–1123.
- (42) Qian, L. M.; Li, M.; Zhou, Z. R.; Yang, H.; Shi, X. Y. *Surf. Coat. Technol.* **2005**, *195*, 264–271.
- (43) Kopta, S.; Salmeron, M. *J. Chem. Phys.* **2000**, *113*, 8249.
- (44) Bennewitz, R.; Dickinson, J. T. *MRS Bull.* **2008**, *33*, 1174–1180.
- (45) Katsuki, F. *J. Mater. Res.* **2009**, *24* (1), 173–178.
- (46) Katsuki, F.; Kamei, K.; Saguchi, A.; Takahashi, W.; Watanabe, J. *J. Electrochem. Soc.* **2000**, *147* (6), 2328–2331.

- (47) Maw, W.; Stevens, F.; Langford, S. C.; Dickinson, J. T. *J. Appl. Phys.* **2002**, *92* (9), 5103–5109.
- (48) Vigil, G.; Xu, Z.; Steinberg, S.; Israelachvili, J. J. *Colloid Interface Sci.* **1994**, *165*, 367–385.
- (49) Zhou, Z. F.; Li, K. Y.; Bello, I.; Lee, C. S.; Lee, S. T. *Wear* **2005**, *258*, 1589–1599.
- (50) Zhu, T.; Li, J.; Lin, X.; Yip, S. *J. Mech. Phys. Solids* **2005**, *53*, 1597–1623.
- (51) Freiman, S. W.; Wiederhorn, S. M.; Mecholsky, J. J. *J. Am. Ceram. Soc.* **2009**, *92* (7), 1371–1382.