Effect of surface hydrophilicity and water vapor pressure on the interfacial shear strength of adsorbed water layer

Doo-In Kim and Hyo-Sok Ahn
Tribology Research Center, Korea Institute of Science and Technology, 39-1 Havolgok-dong, Songbuk-gu, Seoul 136-791, Korea

Dong-Hoon Choi
School of Mechanical Engineering, Hanyang University, 17 Haengdang-dong, Seongdong-gu, Seoul 133-791, Korea

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We investigated the effect of water vapor pressure and surface hydrophilicity on the tribological behavior in wearless sliding condition. Friction and interfacial shear strength of silicon surfaces with different water affinity (contact angles of <5°, 30°, and 85°) against a glass sphere (contact angle 40°) were examined under various water vapor pressure conditions. The friction of hydrophilic surface decreased as vapor pressure increased and the least hydrophilic surface showed stable and low friction force regardless of relative vapor pressure. However, it showed that the hydrophilic surface with high relative vapor pressure exhibited lower shear strength than a less hydrophilic surface independent of capillary effect. It was explained in terms of capillary wetting and the role of adsorbed water in contact area. © 2004 American Institute of Physics.

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Adhesion, friction, and wear at the micro- and nanoscales are currently the subject of intense research to understand the origin of friction and to improve the reliability of micro- and nanoelectromechanical systems. In a lightly loaded wearless sliding contact between well-defined surfaces, interfacial friction force \( F_f \) appears to be proportional to a shearing contact area \( A \).\(^1\) The contact area calculated based on a conventional adhesive contact theory such as the Johnson, Kendall, and Roberts\(^2\) model is inadequate for the micro- and nanoscale sliding contacts because capillary wetting has a strong effect on the contact in humid air.\(^3\) Despite numerous experimental studies employing atomic force microscope to evaluate adhesion property (pull-off force) and friction between a probe tip and a sample surface, there has been a lack of consistency in the explanation of the capillary effect on the contact in relation to relative humidity and water affinity of the surface. Capillary force was shown to be dominant among adhesion forces in humid air and it varied as a function of relative humidity.\(^4\) Therefore, hydrogen-terminated organic molecular films, which show strong hydrophobic property, have been believed as the most promising boundary lubricants for low friction by reducing capillary condensation.

On the other hand, water molecules are readily adsorbed on a solid surface exposed to humid air and confined in the shearing contact area even before a relative motion occurs.\(^5\) This thin water layer is known to reduce friction as it behaves like a boundary lubricated layer.\(^6\) Even though the shearing property of adsorbed water in the contact area may not conform to dynamics of confined liquid film as the water layer has only one or two monolayers thickness,\(^7\) the layer may prevent direct solid-solid contact and, thereby, changes the shear strength at the contact interface \( F_f/A \). Consequently, condensed water has both beneficial and detrimental effects on interfacial friction. In this letter, we investigated the influence of water condensation on friction behavior and interfacial shear strength as a function of water vapor pressure for silicon surfaces with different water affinity.

We prepared three types of silicon surface with different water affinity by controlling silanol (Si–OH) group which has strong interaction with water. Highly polished silicon (100) wafers, covered with a native oxide layer of 1 nm thickness, were cut in pieces of 12×12 mm\(^2\) before modification. This bare Si sample was used as an intermediate hydrophilic (IH) surface after sequentially cleaning in an ultrasonic bath with acetone and methanol for 15 min each. A least hydrophilic (LH) surface was obtained by immersing the bare Si sample into a 40% aqueous solution of hydrofluoric acid for 5 min. This treatment is known to remove the native oxide layer and terminate the surface by mainly Si–H, rendering the surface hydrophobic.\(^8\) The most hydrophilic (MH) surface was prepared by heating the bare Si sample in \( \text{H}_2\text{O}:\text{NH}_4\text{OH}:\text{H}_2\text{O}_2 \) mixture (7:4:1, in vol.) at 320 K for 15 min. This hydrophilization treatment removed adsorbed contaminants and built up additional silanol group. The modified surfaces were rinsed with distilled water and dried under a stream of dry nitrogen. The x-ray photoelectron spectroscopy (XPS) analysis and contact angle measurement were performed to confirm the water affinity. Evaluation of friction behavior was performed using a custom-built microtribometer in a humidity control chamber. Various vapor pressure conditions (0.1–0.8 with 0.1 increment) were adjusted by a hygrometer (0–90±2.5%) and de-ionized water vapor. We used 3-mm-diam glass spheres, as the counterpart in the friction test, prepared in the same protocol as the IH surface. The contact angle of glass sphere was ~40° and the micro-roughness (rms) was less than 1 nm within the scanning area.
of 2 × 2 μm² measured by an atomic force microscope. The glass sphere was oscillated against a stationary plate with an applied load of 300 mN (F_{mech}). The sliding speed was 330 μm/s and the stroke was 1.6 mm.

Figure 1 shows XPS spectra of the Si 2p region for the modified surfaces. Si 2p doublet peaks (binding energy ~99.2 and 99.8 eV) were dominantly detected in all surfaces whereas the peaks for SiO (102.3 eV) and SiOH (103.3 eV) in MH and IH surfaces were observed. The peak analyses showed that the MH surface had a higher peak ratio of SiOH/SiO in comparison with the IH surface with an additional SiOH peak ~100.4 eV. However, these peaks were completely removed on the LH surface due to the removal of oxide layer. XPS analysis revealed that the silanol group on the surface was successfully controlled as expected. The contact angle measurement further confirmed the level of hydrophilicity of the surfaces: 5°, 30°, and 85° for MH, IH, and LH surfaces, respectively.

Figure 2 presents the results of friction measurement for each surface as a function of relative vapor pressure. The friction of the LH (85°) surface was low and stable, and independent of water vapor pressure while the MH (<5°) and IH (30°) surfaces were markedly influenced by water vapor pressure. This result confirmed the general observation that friction is proportional to surface hydrophilicity.

We therefore suggest that the water molecules adsorbed in the contact area may play a crucial role in the friction between two hydrophilic surfaces. We adopted the Hertz model with capillary condensation proposed by Fogden and White in order to investigate interfacial shear strength. In our model, we assumed that the condensed water enabled the formation of meniscus around the contact area with negative Laplace pressure by Kelvin equation and, in addition, the adsorbed water molecules were simultaneously confined in the contact area, thereby preventing direct solid–solid shearing (Fig. 3). With given geometric approximation and assumption of circular meniscus free surface, the meniscus height (S) is given by

$$ \frac{\gamma_L V}{RT \ln(P_v/P_s)} = r_K \approx \left( \frac{1}{r_1} + \frac{1}{r_2} \right)^{-1} \frac{1}{\cos \theta_1 + \cos \theta_2} S, $$

where $\gamma_L$ is the liquid–vapor surface tension, V the molar volume, R the gas constant, T the temperature, $P_v/P_s$ the relative vapor pressure, and $\theta_1, \theta_2$ the contact angle of surfaces. Considering the interatomic distance and the characteristic dimension of water molecule (~2.5 Å), and taking into account the unavoidable uncertainty in determining the thickness of the confined water layer, the minimum separation between two surfaces was assumed as 3 Å. The capillary force is given by multiplication of Laplace pressure ($\gamma_L/r_K$) by meniscus area ($\pi(r_2^2 - a^2)$). The convex radius of meniscus, $r_2$, can be obtained by a numerical iteration process.
first calculated the initial value of $r_2$ from the Hertzian deformation profile, 15 $d(r)$, by the mechanical loading which satisfied $d(r) = S - d_0 = R (\cos \theta_1 + \cos \theta_2) - d_0$ at a given relative vapor pressure assuming $r_1 \approx r_K$. The deformed geometry was then updated by considering a combined loading (a sum of calculated initial capillary force and the mechanical loading). Then new values of $d(r)$ and $r_2$ were obtained which in turn caused a change of the capillary force. The deformation profile was accordingly updated again due to the change of combined loading. This iteration process continued until the capillary force converged. The interfacial shear strength was derived from measured friction force and calculated shearing area.

Figure 4 indicates that the theoretical capillary forces were one order of magnitude greater than the mechanical loading ($F_{\text{mech}}/r_{sp} = 0.2 \, \text{N/m}$) and thus capillary force mainly contributed to the elastic deformation of the MH and IH surfaces. The $F_{\text{cap}}/r_{sp}$ values calculated in this study are greater than those calculated by only considering the capillarity without deformation of the solids and separation (0.75 and 0.81 N/m for IH and MH surfaces, respectively), 13 and in good agreement with the experimental study conducted by Crassous et al. 16 The increase of capillary force as relative vapor pressure increased to its critical value (~0.3) is attributed to the increase of effective area for meniscus formation. Further increase of vapor pressure up to near saturation state led to a decrease of capillary force due to a decreased chemical potential in spite of the increase of meniscus area. 3 As for the LH surface, the meniscus was not formed in this model because the meniscus height calculated was smaller than the thickness of the confined water layer. Figure 4 shows that shear strength behaved similar to experimental friction behavior except for the LH surface. The lower shear strength of the more hydrophilic surface than that of the less hydrophilic one beyond the relative vapor pressure of approximately 0.3 suggests that interfacial shear strength was more dominantly influenced by the confined water layer than capillary force. It seems that the more hydrophilic, the easier shearing of the confined water layer. However, at lower relative vapor pressure (<0.3), the marked increase of the shear strength of hydrophilic surfaces (MH and IH) was attributed to the strong influence of capillary force. However, one can notice that the shear strength of hydrophilic surfaces (MH and IH) continuously increased with the decrease of relative vapor pressure despite the significant decrease of the capillary force, indicating that partial solid–solid shearing due to inhomogeneity of adsorbed water 17 in the shearing interface played a crucial role in increasing the shear strength.

In summary, we examined the effect of the hydrophilicity of surface on friction and shear strength in the wearless sliding condition. The friction force of hydrophilic surface decreased as the vapor pressure increased. In particular, the least hydrophilic surface showed a stable and lower friction force regardless of relative vapor pressure. More hydrophilic surface with high relative vapor pressure exhibits lower shear strength than less hydrophilic surface independent of capillary force due to the role of adsorbed water in the shearing area. The influence of hydrophilicity on shearing dynamics of adsorbed water in the contact area is, however, still unclear. Further investigation is needed in this regard for the better understanding of the shear strength effect on wear initiation and enhancement of boundary lubricants for micro- and nanosystem.

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