Effect of Capillary Force on Friction Force Microscopy : A Scanning Hydrophilicity Microscope

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The effect of capillary force due to surface water on friction force microscopy (FFM) was examined by comparing FFM images on oxidized Si surfaces partially covered with chemically bound hydrocarbon (HC) monolayers *in vacuo* and in an ambient atmosphere. It was found also from force-distance curves and FFM under various relative humidities that adhesive and friction forces observed on the hydrophobic HC covered surface were almost independent of the humidity, while those on the hydrophilic bare oxidized Si surface increased with an increase in the humidity. The higher friction observed on the oxidized Si in the higher humidity was interpreted by the higher effective normal load due to the higher capillary force which originated from a surface water film formed by adsorption of water vapor in the humid air. The results suggest a novel scanning hydrophilicity microscope under a controlled humidity which can be used to map local hydrophilicities of a sample surface in a x-y plane.

Previously,[1-4] it was demonstrated that a friction force microscope (FFM),[5-7] where both the normal and lateral forces were measured simultaneously during atomic force microscopy (AFM),[8] can be used to differentiate distinctly different chemical species on a molecular scale. The mechanism of contrast in friction has, however, not been clarified yet completely. The difference in adhesive forces[9] between the tip and the different chemical surfaces can be one of the most possible mechanisms.

Recently, it was observed,[10] however, from FFM on the Langmuir-Blodgett (LB) films that, even on the same material, different states of the monolayers showed different friction forces. In other words, chemical differentiation only by the relative intensities in friction is unreliable if one does not take into account the physical states of the monolayers such as the surface densities. The difference in rigidity due to the different densities may result in the change in the contact area under a constant normal force and thus in the observed friction force. Not only the change in the average densities in the homogeneous monolayer described above, but also the change in the sliding directions on an anisotropic monolayer[11] exhibited different frictions.

More recently, enormous difference in friction was observed in an FFM image of an oxidized Si surface partially covered with the chemically bound HC monolayer.[12] An enhanced adhesive force, $\boldsymbol{F}_{\mathrm{ad}}$, due to water capillary force, $\boldsymbol{F}_{\mathrm{cap}}$, on the hydrophilic oxidized Si surface was expected to act as a predominant component of an effective normal load, $\boldsymbol{F}_{\mathrm{enl}}$, which is the sum of a cantilever bending force, $\boldsymbol{F}_{\mathrm{can}}$, and $\boldsymbol{F}_{\mathrm{ad}}$ as shown in Fig. 1(a). The smaller $\boldsymbol{F}_{\mathrm{cap}}$ and thus the much smaller $\boldsymbol{F}_{\mathrm{enl}}$ was also expected on the HC covered surfaces during the friction measurement, in which $\boldsymbol{F}_{\mathrm{can}}$ was kept constant under a so called constant force mode. The enormous difference in $\boldsymbol{F}_{\mathrm{enl}}$ due to surface water[13] was considered to be the most probable candidate for the observed contrast in friction.

In the present work, this contrast mechanism in friction was examined by comparing FFM on the same chemically modified surface *in vacuo* and in various relative humidities.

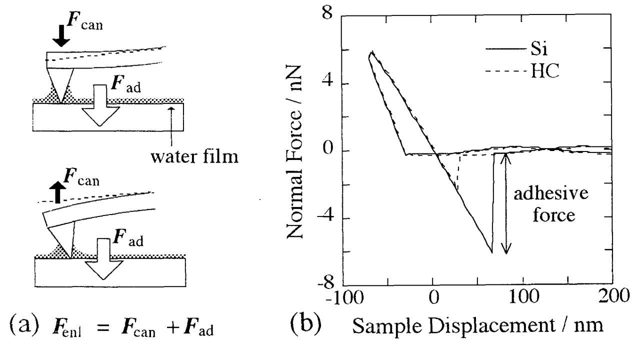

Figure 1. (a) The enormous capillary force, $\boldsymbol{F}_{\mathrm{cap}}$, as a component of the effective normal load, $\boldsymbol{F}_{\mathrm{enl}}$, on hydrophilic surfaces in the humid air and (b) force-distance curves on a HC covered (- - - -) and a bare oxidized Si surface (——) in the humid air.

The chemically modified surface with pattern was prepared by depositing a phase-separated mixed monolayer of carboxylic acid with a partially fluorinated carbon (FC) ($C_9F_{19}C_2H_4OC_2H_4$-COOH, PFECA)[1] and octadecyltrichlorosilane ($C_{18}H_{37}SiCl_3$, ODTCS)[14] on an oxidized Si wafer by the Langmuir-Blodgett method[15,16] followed by heating overnight at 80 °C and sonication in ethanol. The bare oxidized Si surface was exposed by removing the physically adsorbed PFECA domains, but the chemically bound HC monolayer domains remained even after sonication as clearly shown in an AFM image of the chemically modified surface in Figure 2(a), which was recorded simultaneously with an FFM image shown in Figure 2(b) by a Seiko HV-AFM unit with an SPI-3700 control station in the air. An Olympus rectangular cantilever with a normal spring constant of 0.09 N m^{-1} with a Si_3N_4 pyramidal tip was used. The height of the HC do-

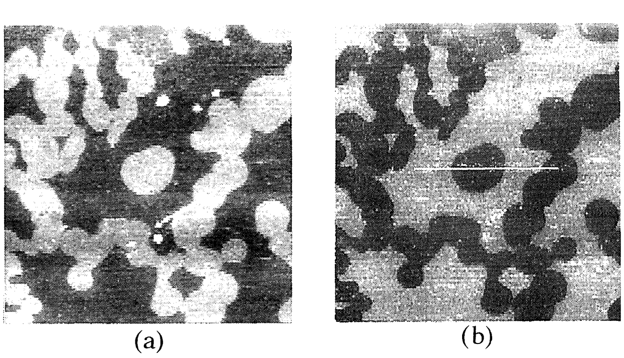
(a) (b)

Figure 2. (a) An AFM and (b) an FFM image (4x4 μm^2) of an chemically modified surface.

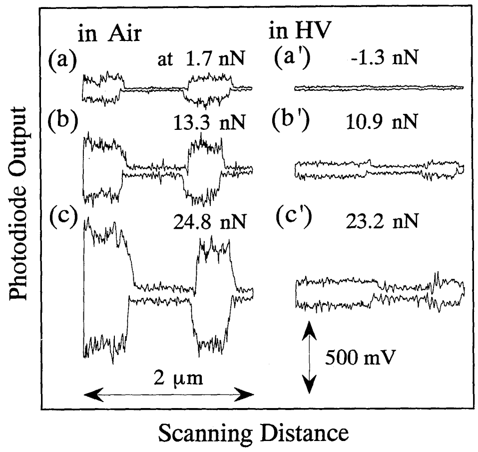

Figure 3. Friction force loops of the chemically modified surfaces in the air and *in vacuo* at different F_{can}.

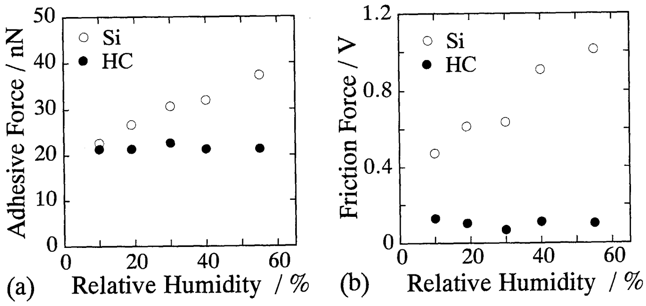

Figure 4. (a) Adhesive and (b) friction forces as a function of relative humidity on the bare oxidized Si (o) and the HC covered (●) surfaces on the chemically modified surface.

mains of ca. 2.2 nm shows that the HC layer was a monolayer. The much higher friction was observed on the topographically lower domains than on the topographically higher HC covered domains.

To confirm the desorption of the physically adsorbed PFECA monolayer, the force-distance curves was measured in the air on the topographically higher and lower surfaces as shown in Figure 1(b). The difference in slopes during approaching and separating the sample surface from the tip is ascribed to hysteresis of a tube scanner. The much higher adhesive force, which was almost the same as that observed on an unmodified oxidized Si surface, is seen in the curve measured on the topographically lower surface. This result indicates that the bare oxidized Si surface was exposed by sonication.

In Figure 3, friction force loops recorded in the air along a line shown in Figure 2(b) are compared with those observed *in vacuo* of 7×10^{-4} Pa with the same tip along almost the same line as shown in Figure 2(b) at three different F_{can}. About two times higher frictions than those on the HC surface were observed on the bare oxidized Si surface *in vacuo*. The difference in friction, however, was much higher in the air. On the HC surface, F_{enl} in Figures 3(a), 3(b), and 3(c) can be considered to be almost the same as those in Figures 3(a'), 3(b'), and 3(c'), respectively, because almost the same adhesive forces were measured in the air and *in vacuo* on this surface. With an increase in F_{can}, both of the frictions increased. But, the frictions observed on the HC surface were almost independent of the atmospheres as long as F_{can} was the same. In contrast, the friction observed on the bare oxidized Si surface strongly depended upon the atmospheres, that is, the much higher frictions were observed in the air than *in vacuo*. The difference in friction can be attributed mainly to the much higher adhesive force on the bare oxidized Si surface in the air than *in vacuo*. The lowered friction and the adhesive force *in vacuo* were recovered by exposing the surface again in the air.

The experimental result described above concerning the effect of evacuation strongly indicates that the friction of the hydrophilic surface increased drastically in the air by the increase in F_{enl} due to F_{cap} ascribed to the presence of water on the surface. As the relative humidity was already known to affect lateral conductivity of ultrathin water films on hydrophilic surfaces such as glass and mica,[13] the adhesive and friction forces were measured on the present chemically modified surface with a different Si_3N_4 pyramidal tip from that used in Figures 1(b) and 3 in various controlled humidities. The results observed on the bare oxidized Si and the HC covered surfaces with this tip are plotted as a function of the relative humidity in Figures 4(a) and 4(b). The friction in Figure 4(b) was measured under zero F_{can}. Thus, F_{enl} is considered to be equal to F_{ad} on each surface because of zero F_{can}. As shown in Figure 4(a), F_{ad} on the HC surface was almost independent of the humidity, while that on the bare surfaces increased with an increase in the humidity. Coincidence of F_{ad} observed on both surfaces under zero humidity seems to be accidental.

As shown in Figure 4(b), almost the same tendency was observed for the friction as a function of the humidity. But, the much higher difference in the frictions between the bare and the HC surfaces was observed than that in F_{ad} shown in Figure 4(a). The enhanced effect of the humidity for the friction can be ascribed mainly to the higher friction coefficient on the bare surface than that on the HC surface, although dependence of frictions on F_{enl} observed on both surfaces is not shown here.

In conclusion, the observed high contrast in the friction force in a high humidity or the humidity dependence of the friction can be used to map local hydrophilicities on various surfaces as well as those for F_{ad}. In addition, true difference in frictions inherent to chemical interactions between different sample surfaces and a tip surface should be deduced by FFM *in vacuo* by taking account of the change in contact area caused by the change in physical states. For precise friction measurements, chemical modification of AFM tips is also required.[4]

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