Large oscillatory forces generated by interfacial water under lateral modulation between two hydrophilic surfaces

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(Received 12 September 2011; accepted 22 October 2011; published online 14 November 2011)

We observed remarkable oscillatory forces with amplitude of 60-90 nN and periodicity of 3–4 water molecule diameters in an ambient environment between two silicon surfaces as the tip-sample distance decreased using the cantilever-based optical interfacial force microscope with lateral modulation. As the humidity increased, the oscillatory forces changed from being large at lower relative humidities, below 40%, to progressively becoming smaller as the humidity went higher than 40%. The frequency of oscillatory forces increased with the existence of lateral tip-modulation and with the slower approaching tip-speed. Its starting point distance has been found to originate from the topographic water structure. © *2011 American Institute of Physics*. [doi:10.1063/1.3662008]

Oscillatory forces have been routinely observed at the interface between a hydrophilic surface (e.g., silicon, mica, etc.) and bulk water.[1–3] Over the past decade, studies using atomic force microscopes (AFM) at the liquid-solid interface have found that the interfacial water confined between two surfaces forms water layers with periodicity of a single water molecular diameter such as 0.22,[1] 0.25,[2] and 0.22-0.27 nm.[3] Molecular forces due to the transition between ordering and disordering states, depending on the commensuration and incommensuration between the spacing and the molecular diameter,[4] can explain the observed periodicities. However, a previous study in an ambient environments where vapor, solid, and liquid co-exist, showed that there was different periodicity from those at the liquid-solid interface.[5] The periodicity was observed to be 0.6-1.2 nm in the water bridge formed at the relative humidity (RH) of 15%.[5] More measurements are necessary to understand the origin of the deviation in periodic forces in the ambient environment. These studies have used techniques measuring force derivative to avoid mechanical instabilities of the tip-sensor assembly called the "snap-to-contact" problem[6] associated with most widely used AFM techniques. Measuring static forces instead of force derivatives would be ideal for comparison with existing theories.[4] As a way to measure static forces while avoiding the mechanical instability, we recently developed a cantilever-based optical interfacial force microscope (COIFM) and thus demonstrated large sawtooth-like oscillatory forces generated by interfacial water molecules under a lateral modulation between two hydrophilic surfaces.[7,8] In this paper, we investigate the large oscillatory forces through four different control measurements including topographic imaging, speed, RH, and changes in lateral modulation to find their nature and relevance with the interfacial water.

The experimental setup consisted of a lateral modulation technique incorporated into the existing COIFM to measure lateral forces as well as normal forces.[8] This lateral modulation has been achieved by applying an ac-modulation signal to the +/− x-electrodes of the piezotube scanner. The feedback voltage applied to the ZnO stack of a commercially available "dimension micro-actuated silicon probe" (DMASP) sensor in response to the detection signal is the output signal for the measurement of forces acting on the cantilever.[9] The dc and ac components of the output signal were simultaneously recorded using a lock-in amplifier (7225 DSP, Signal Recovery, Oak Ridge, TN). The two components were recorded as a function of distance and converted into forces using conversion factors of 18.51 and 222.13 nN/V for normal and lateral force, respectively.[8] The sample surface used was a silicon wafer Si(100) (SPI Supplies, West Chester, PA) that was cleaned using a piranha solution made from a 3:1 concentration of H_2SO_4/30% H_2O_2 (Pharmco and Fischer Scientific, respectively). It was then sonicated in acetone for 5 min, then ethanol for 5 min, rinsed with DI water, and then dried with a dry N_2 flow. Subsequently, we measured the contact angle using the static sessile drop method with distilled water.[10] The contact angles are found to be 17°–42°, which is consistent with many known literature values of clean silicon surfaces (e.g., Ref. 11). When topographic images were taken on the same surface by contact-mode AFM, they were found to be smooth (less than 0.3 nm) without any appreciable features within scan areas on the surface.[10] The tips and the samples then were cleaned using a UV sterilizer (Bioforce Nanosciences Inc., Ames, IA) to remove any possible residual hydrocarbon molecules. The tip approached the freshly cleaned silicon at the tip speed of 8 nm/s and with lateral modulation amplitude of 0.6 nm at a frequency of 1 kHz. All measurements were performed in an ambient environment at varying RH values at room temperature of 22 °C.

The force-distance curves show oscillatory forces in both normal (red) and lateral frictional (blue) force (Fig. 1(a)). The tip started to interact with interfacial water molecules at 17 nm away from the surface. Once the tip and sample came in contact, there was a very sharp change in normal force and an increase in friction force as well. The oscillatory amplitude in normal forces is 60–90 nN with a periodicity of 1.001 nm ± 0.188 nm and 0.961 nm ± 0.185 nm for valley-valley and for peak-peak distances, respectively. This

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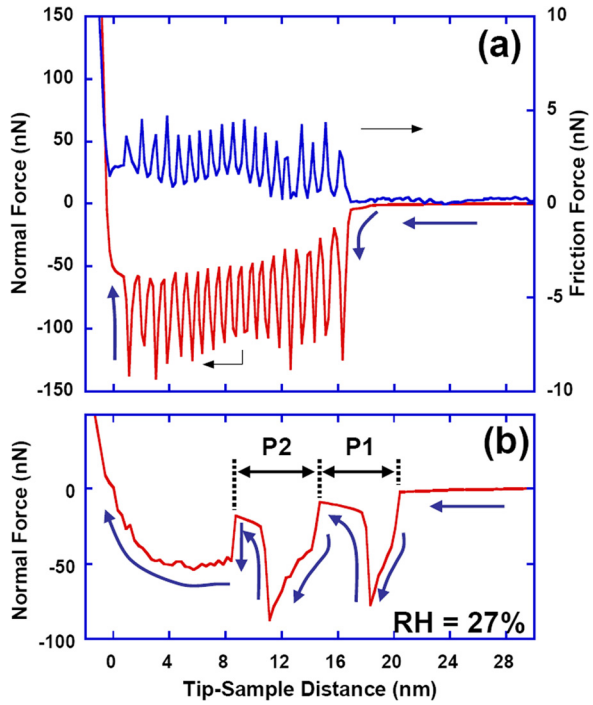

FIG. 1. (Color online) (a) Force-distance curves collected using COIFM with lateral modulation of 6 nm at RH 33%. Both normal and lateral forces show large oscillatory forces generated by interfacial water molecules confined between two hydrophilic surfaces in air. (b) Force-distance curves measured without lateral modulation at RH 27%. The oscillation period is increased by several times. P1 and P2 represent the period of oscillation. The segment after P2 is the transitional interval from oscillatory to repulsive force by the sample surface.

periodicity is roughly three diameters of water molecules (diameter of single water molecule is ~0.3 nm). The periodicity of multiple water molecule diameters, instead of one water molecule diameter, suggests that the interfacial water structure in the ambient environment is possibly different from the solid-liquid interface. This periodicity of multiple water molecule diameters is consistent with the earlier observation.[5]

We excluded the possibility that the large oscillatory force might be generated by the tip-sample (or adsorbed water layer) interaction due to the z-displacement induced by the lateral modulation. Since the z-displacement due to the lateral motion is known to be ~0.1%, the z-motion is estimated to be in the 0.6 pm range for 6 nm modulation in the x-direction.[12] The effect of this subpicometer z-movement on the forces is almost negligible, as the appreciable force change occurs at the nanometer length scale in Fig. 1(a). In addition, because the modulation frequency is 1 kHz, the response frequency should be the same if there is a coupling between lateral modulation and z-motion. However, the frequency of the sawtooth pattern (~8 Hz) is far below the modulation frequency. Furthermore, the same periodicity in normal force as that in frictional forces extracted from the lock-in output in Fig. 1(a) does not show that the normal force resulted from the modulation signal itself.

To investigate the influence of the lateral modulation on the periodicity, normal force-profiles were measured without modulation. The periodic features were reduced remarkably, only two oscillations in the distance between 0 and 20 nm, as denoted as P1 and P2 in Fig. 1(b). The absence of modulation results in the decrease of the number of oscillations by several times, increasing the periodicity from 0.9 to 6 nm. If the transition is a kinetically activated process, it should be a time-dependent process. The force-profile (Fig. 2) shows that the oscillatory periodicity increased from 0.9 to 6 nm when the tip speed is changed from 8 to 27 nm/s. More measurements support this idea, as shown in the inset of Fig. 2, where the periodicity increases with tip-speed. The observed time-dependent transition is suggestive of a kinetically activated transition process consistent with an earlier report in the friction measurements at the capillary junction.[13] The periodicity increase due to the lateral modulation (observed in Fig. 1(b)) is explainable by the kinetic energy promoting layering transitions by overcoming the activation barriers between two successive layered states of the interfacial water. Similar effect of force excitations has been observed on atomic scale friction.[14]

Force-profile measurements were conducted as a function of ambient humidity to find how the oscillatory force is dependent on the volume of water molecules confined between the two surfaces. The COIFM was placed in an acrylic box with one entrance for water vapor and another for dry nitrogen gas. Relative humidity was altered by controlling the amount of vapor and dry gas that flowed into the box and was monitored using a thermo-hygro recorder (Control3, Friendswood, TX). The measurement at the next RH value was performed after approximately one hour from the point of the change to have sufficient saturation time. Figure 3 shows the force-distance profiles measured without lateral modulation when the relative humidity changed from 22 to 72%. Again, large oscillations were observed below 40%, whereas the oscillation decreased remarkably above 40%. This strong humidity dependence of the oscillatory forces indicates that there could be a structural phase transition of water. This idea is supported by the sudden decrease of the starting distance from around 20 nm at lower RH to around 16 nm at higher RH (as shown by the arrows). It appears that the water structure at the lower humidity is extended farther away from the surface than those of higher humidities. These humidity dependent oscillatory forces confirm that they originated from water molecules and not from experimental artifacts.

Topographic imaging was performed on the surface using non-contact mode AFM to understand the origin of these starting distances in the force profiles.[15] Figure 4(a) shows

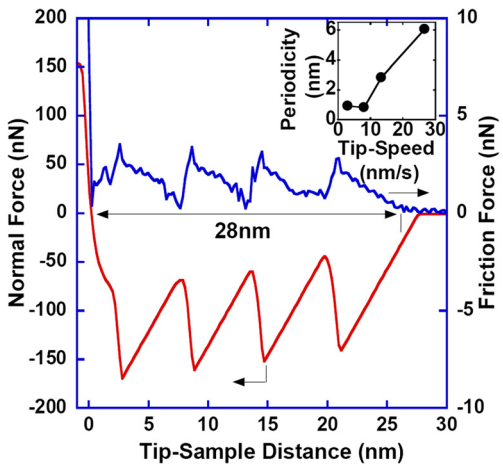

FIG. 2. (Color online) Measurement taken at a lower time-scale of 30 s at a tip-speed of 27 nm/s at RH 33%. (inset) The periodicity in relation to the varying tip-speeds.

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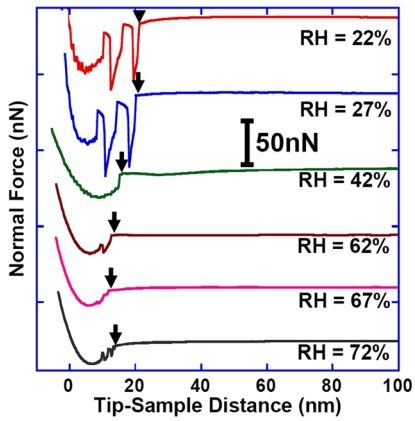

FIG. 3. (Color online) Force-distance curves with different RH values without lateral modulation at a tip-speed of 8 nm/s. The oscillatory force decreases drastically at humidities above RH 42%. The arrows point to the distance where two water structures meet between the two surfaces.

water molecular structures formed on the terraces separated by a step of the silicon surface taken at RH 47%. The water structures are more corrugated between roughly 2 and 10 nm over the entire terraces, as shown in a sectional profile (Fig. 4(b)) made along the line displayed on the image. At varying locations, there exist some elongated water structures, as marked with arrows. These structures are significantly different than thin-layered structures, with a thickness less than a few nanometers on a clean hydrophilic mica surface.[15,16] As the elongated water structures should be adsorbed partially on both tip and sample surfaces at humidities below 40%, the onset distance where forces started to change should appear when the water structures of both surfaces begin merging together. Neither of the surfaces had to be fully covered with thin water layers of less than ~2 nm. Any additional forces, such as dragging forces, are not required to explain this long-range onset distance. Therefore, the direct touching between water molecules on the two surfaces should be the origin of the observed onset distance of ~20 nm away from the surface. The topographic heights agree with the starting point in the force-curves, as tall features are ranged between 8 and 10 nm high. The small portion of the tall features should be sufficient to generate observed 60–90 nN. For example, the sectional widths of 8–10 nm features are found to be approximately 20–40 nm, which corresponds to 3300–13 000 water molecules within the sectional plane. This number produces the force corresponding to 20–70 nN force, assuming a typical H-bond force of 5 pN per hydrogen bonds.[17]

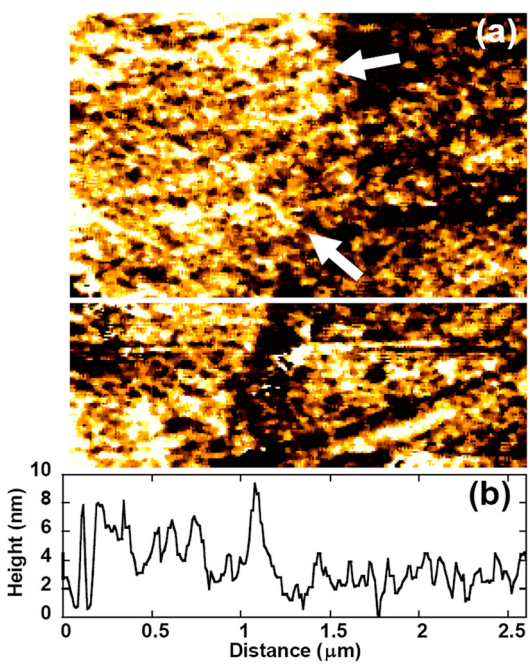

FIG. 4. (Color online) (a) Non-contact AFM image of water structures on the silicon surface at RH = 47% (scan area: 2.5 μm × 2.5 μm). (b) A sectional profile along the white line above shows that water clusters are up to 8–10 nm high.

In summary, oscillatory forces are dependent not only on the relative humidity, but also on the existence of lateral sample modulation and the approaching speed. The lateral modulation and speed dependence is consistent with the thermally activated process proposed by an earlier study by Riedo *et al.*[13] The result suggests that the COIFM technique using lateral modulation may provide a unique opportunity to reveal the interfacial water structure, potentially overcoming a significant barrier faced by the current scanning probe techniques. The information could be used to establish a quantitative theory about the interaction between water molecules and hydrophilic surfaces, such as silicon oxide. It can also contribute to liquid-based nano and bio-technologies as well as to the improved performance of moving components in silicon-based micro-electro-mechanical system devices where water molecules play a key role in interfacial interactions.

This research was supported by NSF DBI-0852886, NSF DMR-1126854, NSF EPSCOR Startup Augmentation Funding, and the Research Corporation Single-Investigator (Cottrell College Science Award No. CC7041/7162).

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