Frictional and Adhesive Properties of Diamond-like Carbon/ Silicon Nitride Nanocontacts

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ABSTRACT

Diamond-like carbon (DLC) is a unique material that exhibits both low friction and high hardness. This material is being considered as a coating for a wide range of applications, including micromachines, where friction and adhesion play a critical role in performance. In the present study, we seek to understand more fully the fundamental relations that govern the tribology of DLC at the nanoscale. In particular, we wish to understand the way in which humidity tends to reduce the superior frictional properties of DLC. Coatings of DLC were deposited on silicon flats using the plasma source ion deposition process. These coatings are studied using atomic force microscopy, where a nanoscale tip is placed in contact with a sample to measure relative adhesive and frictional forces. Dependence of friction and adhesion on relative humidity, load, and sliding history for a DLC/ silicon nitride interface are discussed.

INTRODUCTION

Friction is a ubiquitous physical phenomenon that is not well understood on a fundamental level. Most surfaces are rough on small scales, although macroscopically they may appear smooth. Surfaces that are apparently in complete contact are in fact only in contact at raised points, or asperities, which complicate surface interactions during sliding. The frictional behavior of a single asperity should be studied in order to obtain a clearer understanding of the most basic processes involved. Furthermore, understanding friction and wear on the nanoscale is especially important for the development of devices that work on the micro- or nano-scale, where surface forces dominate [1].

Diamond-like carbon (DLC), an amorphous solid composed of sp^2- and sp^3-bonded carbon, is a useful coating material for many applications. In particular it holds promise for application in micro-electro-mechanical systems (MEMS), since DLC exhibits low friction and high hardness [2]. The frictional properties of DLC depend strongly on environmental humidity, whereby the superior low friction behavior wanes at higher humidity. The mechanisms that govern the relationship between friction and humidity for this material are not well understood. This paper presents a characterization of DLC film behavior in a humidity-controlled environment.

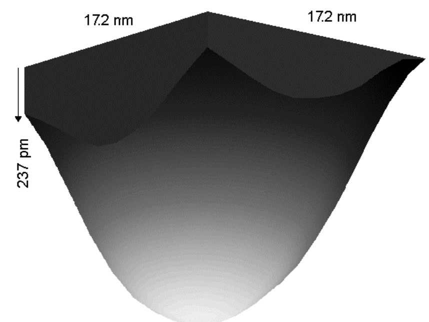

Figure 1: A correlation average from the tip calibration sample, which gives an approximation of the tip shape.

EXPERIMENTAL PROCEDURE

DLC films were deposited on silicon wafers using the non-line-of sight plasma source ion deposition process, developed at the University of Wisconsin-Madison [3]. Atomic force microscopy (AFM) was performed on the DLC to characterize its tribological properties. In AFM a cantilever with a nanoscale tip is brought into contact with a surface. Deflections of the tip and cantilever are measured using a laser beam reflected off the back of the cantilever. The bending and twisting of the cantilever as it moves across a surface provides a measure of normal and friction forces that act between the tip and the sample with sub-nanometer and sub-nanoNewton precision.

A Nanoscope IV AFM (Digital Instruments, Santa Barbara, California) with a silicon nitride AFM cantilever was used for this study. The cantilever used was of rectangular geometry, with a manufacturer's spring constant of 0.05 N/m for cantilever bending. Batch processing of AFM cantilevers by chemical vapor deposition causes considerable variation in the cantilever spring constants. Thus, this nominal value allows for the calculation of tip-surface forces only within an order of magnitude.

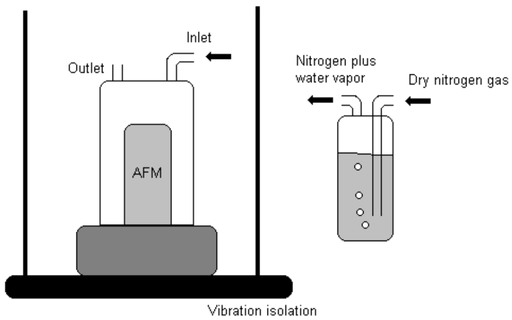

Figure 2. Illustration of the experimental setup for environmental control of relative humidity.

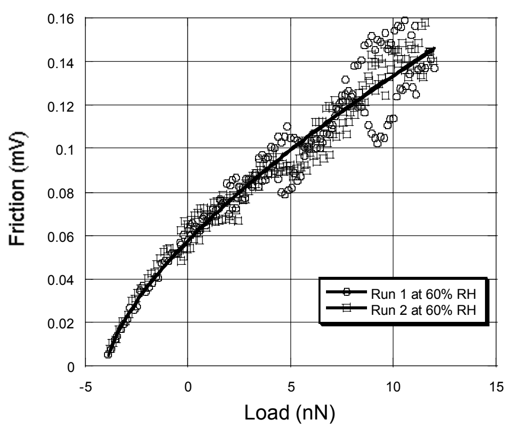

Figure 3. Friction (a.u.) vs. load (nN) for DLC (circles, Run 1; squares, Run 2), with fits of the DMT model (solid lines).

A blind reconstruction of the tip [4] using tip calibration samples (Aurora NanoDevices, Edmonton, Canada) gives an approximate upper bound for the tip radius of 19 nm. This process was achieved using a demonstration version of Scanning Probe Image Processor software (Image Metrology, Aps, Denmark). This AFM tip was tested before and after the experiment, and no significant tip changes were observed to occur during the experiment.

The tip calibration sample used to quantify the tip radius was composed of a random arrangement of sharp spikes with an average radius of curvature of less than 5 nm. When an AFM tip in run over sharp features such as these, the resulting image is nearly an inverted image of the AFM tip. Software was used (RHK Technology, Troy, Michigan) to average the repeated imaged tip from the correlations found over a 400 nm image. An example correlation average is shown in Figure 1. This was not the method by which the radius curvature of the tip was obtained, but it gives a qualitative visual depiction of the form and size of the tip.

The AFM was placed on a platform attached to compliant bungee chords for vibration isolation. Environmental humidity for this experiment was controlled using the setup depicted in Figure 2. A plastic hood separated the AFM from the ambient environment and flowing nitrogen into the hood allowed for control of the hood environment. Humidity variation was accomplished by bubbling nitrogen into deionized water, which caused water vapor to be carried along with the nitrogen into the hood. Manual adjustment of the nitrogen flow rate allowed for humidity control to within a few tenths of a percent. Relative humidity (RH) and temperature were monitored using a digital hygrometer / thermometer. Temperature was found to vary negligibly during the experiment.

The tip was scanned at a rate of 0.3 nm/s across the DLC surface, while the relative tip-sample load was varied using a breakout box to send signals to the AFM controller. The load was ramped from a large positive load and decreased until the tip pulled off of the surface. Then the tip was again brought into contact with the sample and the load increased to return to the starting load to complete one friction versus load curve in 170.7 seconds. These data were acquired at humidities ranging from less than 5% RH to 70% RH, at increments of 10%. This was followed by a reversal back to less than 5% RH to rule out time-dependent effects. At each humidity level the tip was pulled out of contact from the surface and was allowed to equilibrate with its environment for 10 minutes. The shape and range of the friction versus load curves were quite consistent for data taken at each humidity level, indicating that the system had achieved a steady state. No hysteresis was observed in these friction measurements, which also indicates little system variation.

RESULTS AND DISCUSSION

Figure 3 shows the variation of friction with applied load for DLC films in an environment of 60% RH. These measurements were acquired at different times, where the humidity was changed between the measurements and as well additional scanning took place. Between the measurements shown the tip was scanned at 0.3 nm/s for five 50 x 50 nm^2 images which are composed of 512 lines each, for a total scanning length of 128 μm. The time elapsed between the two scans was approximately 90 minutes, for which the tip was actually in contact with the surface for 10 minutes. The data sets overlap extremely closely.

Furthermore, the data are in excellent agreement the Derjaguin-Müller-Toporov (DMT) model, which predicts how contact area varies with load, assuming that the materials are fairly stiff and the adhesion forces long-range [5]. This theory is similar to the Hertz theory of contact [6], except that here unspecified interfacial adhesion gives an offset to the curve so that surfaces separate at a negative force. The DMT model predicts that the contact area *A* should vary with load L as follows:

$$A = \pi\left(\frac{R}{K}\cdot\left(L + L_C\right)\right)^{2/3} \qquad (1)$$

where R is the tip radius, and K is the contact modulus, defined as:

$$K = \frac{4}{3}\left(\frac{1-\nu_{tip}^{\;2}}{E_{tip}} + \frac{1-\nu_{sample}^{\;2}}{E_{sample}}\right)^{-1} . \qquad (2)$$

Here, E and ν represent the Young's modulus and Poisson's ratio of the tip and sample respectively. Finally, L_C is the critical load required to pull the tip off from the surface. Several recent AFM studies have found that the friction force F_f is directly proportional to the contact area for nanoscale single asperity contacts[1,7-14]:

$$F_f = \tau \cdot A \tag{3}$$

where τ is the interfacial shear strength (friction force per unit area). If τ is constant, then a solution for contact area can be directly fit to the friction data. We find that the DMT model fits our data extremely well (Figure 3), which indicates that the measured friction force is directly proportional to the contact area predicted by the DMT theory. This then yields the following relationship between friction and load:

$$F_f = (0.2305 \pm 0.0003) \cdot (L + L_C)^{2/3} \tag{4}$$

where F_f is the frictional force in uncalibrated raw units (voltage output of the AFM sensor) and L is the load in nanoNewtons. The errors quoted refer to the least-squares fitting error averaged between the two fits shown in Figure 3. Note that calibration of the friction force requires a separate detailed procedure that will be carried out in the near future [15]. The pull-off force was averaged for the two runs shown in Figure 3 and was found to be 3.96 ± 0.11 nN. The DMT relation also gives the Dupré work of adhesion W of the interface

$$W = \frac{L_C}{2\pi R}, \tag{5}$$

where R is the tip radius. For DLC, the value of W was determined to be 0.0332 ± 0.001 J/m^2 at 60% RH.

These results are consistent with the existence of a capillary water neck formed between the tip and sample. Carpick *et. al* observed a similar phenomenon, where friction between silicon nitride and mica at 55% RH was also noted to be in agreement with the DMT theory [7]. Fogden and White have theorized that the capillary condensation can produce a DMT-like dependence of contact area upon load for high humidity [16], which was consistent with a similar model by Maugis [17]. They define a dimensionless parameter, k^{-1}, which is a relative ratio of the range of forces to the deformability of the surfaces in response to the attractive forces. According to this formulation, a given contact behaves according to the DMT theory when $k^{-1} << 1$. A small value of k^{-1} indicates that the materials are relatively stiff, and so the capillary acts as an additional applied load without greatly distorting the contact profile from the Hertz solution. Fogden and White define k^{-1} in the following manner:

$$k^{-1} = \frac{2^{\frac{3}{2}}}{3\pi^{\frac{1}{2}}} \frac{2\gamma_{LV} \cdot R^{\frac{1}{2}}}{K \cdot r_k^{\frac{3}{2}}} \cdot \frac{1}{(1 - D_0/2r_k)^{\frac{1}{2}}}, \tag{6}$$

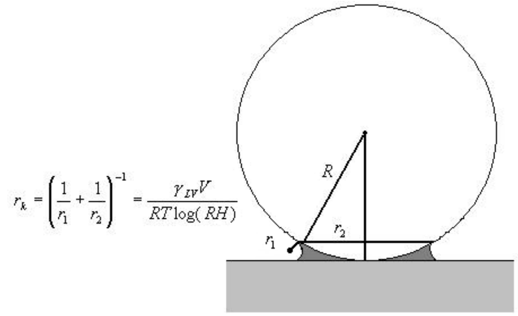

Figure 4. Capillary condensation for a spherical contact.

where γ_{LV} is the surface tension of water at room temperature (72.75 mJ/m^2), r_k is the Kelvin radius, and D_0 is the separation between the two solid surfaces in repulsive contact. The Kelvin radius is a measure of the size of the meniscus that forms between two surfaces. Figure 4 shows the Kelvin radius schematically. D_0 is not measured in our experiment, but it is at least as large as one typical atomic bond spacing, *i.e.* >0.2 nm. k^{-1} is conceptually similar to "Tabor's parameter" raised to the 3/2 power. Tabor's parameter has been discussed previously in the literature as a value that represents the extent to which surface forces locally distort the materials in and near the contact zone [18,19]. In this case, k^{-1} describes the extent to which the capillary distorts the materials near the contact zone. In the limit of small k^{-1}, this effect is negligible and a DMT-like contact area vs. load profile occurs.

For silicon nitride we take ν and E to be 0.27 and 155 GPa [20] respectively. For DLC we take ν and E to be 0.30 and 150 GPa respectively, which are based on previous measurements of similarly prepared DLC films. Finally, we use D_0 = 0.5 nm. For these materials in an atmosphere of 60% RH we find k^{-1} to be $0.000847 << 1$. Note that using smaller values of D_0 would make k^{-1} even smaller. This result confirms our assertion that this interface does in fact fall into the DMT regime at high humidity. We can conclude that water condensed on the DLC surface and the tip strongly influences frictional behavior at this humidity. Further studies are underway to measure the dependence of this effect on humidity variations and contact history.

CONCLUSION

Variation of friction with load was determined at 60% relative humidity. The results were in excellent agreement with the DMT model of contact, which is consistent with the presence of a capillary water neck between the tip and sample. Future studies will investigate the frictional and adhesive properties of DLC as a function of relative humidity.

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