

# The effect of surface chemistry and structure on nano-scale adhesion and friction

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## ABSTRACT

Adhesion and friction are commonly observed to be correlated in many systems, particularly at the nanoscale where adhesion plays a substantial role. In this paper, we examine an unusual *lack* of correlation between nanoscale adhesion and friction. Diamond-like carbon (DLC) is a unique thin film material that can exhibit both low friction and high hardness via easy, low-cost deposition methods. We seek to understand the fundamental relations that govern the tribology of DLC at the nanoscale. In particular, we wish to understand how 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 tip is placed in contact with a sample to measure relative adhesive and frictional forces. We found that friction varies monotonically and reversibly with load, and the dependence can be described extremely well with a Derjaguin-Müller-Toporov model, indicating that we have a single asperity contact, and that friction is directly proportional to the contact area. As the humidity varies from <5% to 60%, friction exhibits a monotonic and reversible change, increasing with higher humidity. In particular, the interfacial shear strength increases by ~40% between our two extremes in humidity. However, we observe absolutely no change in the adhesion force and correspondingly, no change in the work of adhesion. The measurements are carried out at low loads to remain in the regime of elastic contact. This indicates that there is a unique mechanism of friction operating that is not described by conventional pictures invoking a meniscus between the tip and sample, for which adhesion ought to change substantially with humidity.

## 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 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<sup>1</sup>.

Diamond-like carbon (DLC), an amorphous solid composed of sp<sup>2</sup>- and sp<sup>3</sup>-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<sup>2</sup>. The frictional properties of DLC depend strongly on environmental humidity, whereby the superior low friction behavior degrades 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 at the nanoscale using atomic force microscopy (AFM). We study the behavior at the lowest applied loads, to probe mechanisms of friction *before* and wear or damage begins to occur.

## 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<sup>3</sup>. In PSID, the target to be coated is placed in a vacuum chamber, the source gas is introduced, and a plasma of this gas is produced. High-voltage pulses are then applied to the target causing the ions in the plasma to impinge the target surface at normal incidence and deposit a film. The advantage of this non-line-of-sight method is that

coatings can be applied to three-dimensional objects with unusual shapes, including high aspect-ratio AFM tips, although we have only coated silicon flats with DLC for this study.

AFM was performed on the DLC to characterize its tribological properties. 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 normal forces only within an order of magnitude. Even larger errors can result when calibrating the friction forces<sup>4</sup>, and so we provide friction signals in raw data units only (Volts). However, since the *same* cantilever was used for this study, the *relative* comparison between all measurements is meaningful and precise.

A blind reconstruction of the tip<sup>5</sup> using calibration samples (Aurora NanoDevices, Edmonton, Canada) gives an approximate upper bound for the tip radius of 19 nm. The 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.

The AFM was placed on a platform attached to bungee chords for vibration isolation. Humidity was controlled using a plastic hood which separated the AFM from the ambient environment. Nitrogen gas was flowed into the hood to allow for control of the hood environment. Humidity variation was accomplished by bubbling nitrogen through 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 upper positive load and decreased until the tip pulled out of contact from 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 60% 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

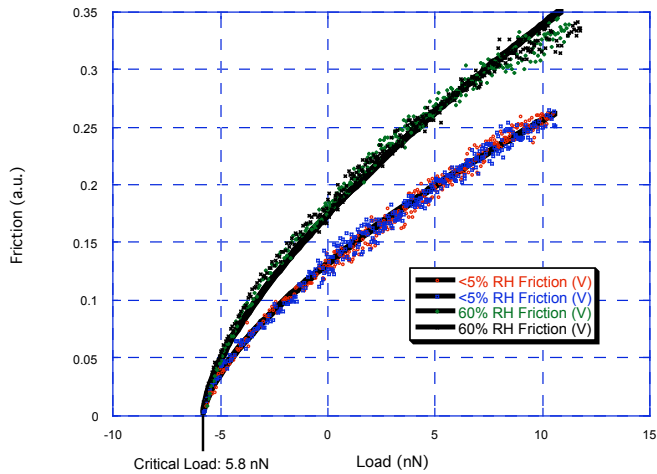
Figure 2 shows the variation of friction with applied load for DLC films in an environment of 5 and 60% RH. A measurement was acquired at 5% RH, then a series of subsequent measurements (not shown in this figure) were acquired. The data overlap extremely closely at each humidity. Friction is clearly higher at 60% RH, but the pull-off force is identical. Figure 3 shows a family of friction vs. load measurements, for which friction is seen to monotonically increase with humidity, but *no variation of the adhesion force is observed*.

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<sup>6</sup>. This theory is similar to the Hertz theory of contact<sup>7</sup>, 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:

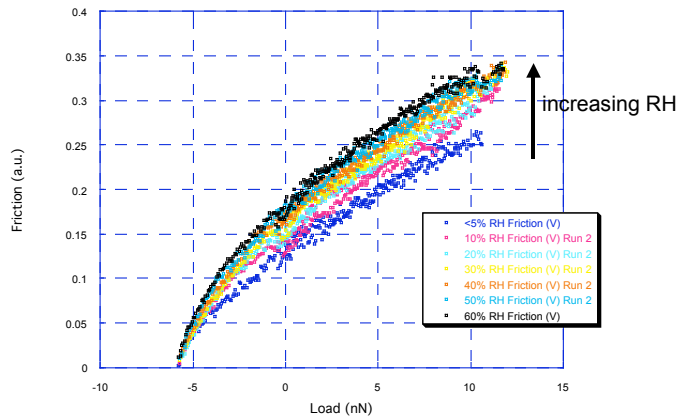
$$A = \sqrt{\frac{R}{K}} \cdot (L + L_c)^{3/2}$$

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

$$K = \frac{4}{3} \frac{\sqrt{E_{tip}}}{E_{tip}} + \frac{1}{E_{sample}} \frac{\sqrt{E_{sample}}}{E_{sample}}$$



**Figure 2.** Friction vs. load at <5% and 60% RH. Solid lines: DMT fits to the data.



**Figure 3.** Friction vs. load from <5% to 60% RH, showing a monotonic increase in friction, but no change in the adhesion force.

Here,  $E$  and  $\nu$  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<sup>1,8-11</sup>:

$$F_f = \tau \cdot A$$

where  $\tau$  is the interfacial shear strength (friction force per unit area). If  $\tau$  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 (solid lines, Figure 3), which indicates that the measured friction force is directly proportional to the contact area predicted by the DMT theory at each humidity. The (uncalibrated, relative) shear strength is plotted as a function of humidity in Fig. 4 and changes by a factor of 1.4 from 5% to 60% RH.

The DMT relation also gives the work of adhesion  $W$  of the interface:

$$W = \frac{L_c}{2R}$$

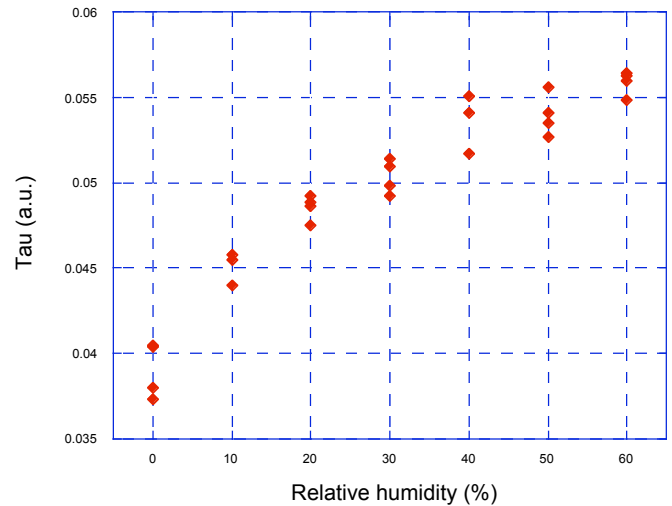
where  $R$  is the tip radius. The average work of adhesion for all the measurements was calculated to be  $0.0547 \pm 0.0004 \text{ J/m}^2$ .

According to classical meniscus theory applied to the humidities and geometry we have in this case, the pull-off force ought to have a substantial variation with humidity<sup>12</sup>. The lack of any change in adhesion indicates that classical meniscus theory fails, in accordance with other recent AFM measurements<sup>13-15</sup>. While the interpretation of the structure and kinetics of water at this scale is speculative at this point, it is possible that a minimum precursor film thickness is required to form the meniscus, and that is not possible on the relatively hydrophobic DLC film at the humidities studies here.

The presence of water molecules nonetheless has a significant effect on friction. There is no experimental technique which can discern the chemistry and structure of water (and any other species) confined at this nanoscale interface *in-situ*. A study using a technique such as molecular dynamics is necessary to understand this behavior in more detail.

## CONCLUSION

Variation of friction with load between silicon nitride and DLC was determined between 5% and 60% RH. We observe an unusual effect where friction increases while the adhesion remains constant. This may be indicative of precursors to damage and high friction in macroscopic contacts involving DLC. Further work studying water on these surfaces are required to understand the nature of this effect.



**Figure 4.** Variation of the (relative) shear strength with relative humidity.

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## REFERENCES

1. Carpick, R. W.; Salmeron, M. *Chemical Reviews* **1997**, *97*, 1163.
2. Erdemir, A.; Donnet, C. In *Modern Tribology Handbook*; Bhushan, B., Ed.; CRC Press: Boca Raton, FL, 2001; Vol. 2.
3. Malik, S. M.; Fetherston, R. P.; Conrad, J. R. *Journal of Vacuum Science & Technology A (Vacuum, Surfaces, and Films)* **1997**, *15*, 2875.
4. Ogletree, D. F.; Carpick, R. W.; Salmeron, M. *Review of Scientific Instruments* **1996**, *67*, 3298.
5. Villarrubia, J. S. *Surface Science* **1994**, *321*, 287.
6. Derjaguin, B. V.; Muller, V. M.; Toporov, Y. P. *J. Colloid Interface Sci.* **1975**, *53*, 314.
7. Hertz, H. J. *Reine Angew. Math.* **1881**, *92*, 156.
8. Carpick, R. W.; Ogletree, D. F.; Salmeron, M. *Applied Physics Letters* **1997**, *70*, 1548.
9. Carpick, R. W.; Agraït, N.; Ogletree, D. F.; Salmeron, M. *Journal of Vacuum Science & Technology B* **1996**, *14*, 1289.
10. Lantz, M. A.; O'Shea, S. J.; Welland, M. E.; Johnson, K. L. *Physical Review B (Condensed Matter)* **1997**, *55*, 10776.
11. Pietremont, O.; Troyon, M. *Surface Science* **2001**, *490*, L592.
12. Carpick, R. W.; Batteas, J. D. In *Handbook of Nanotechnology*; Bhushan, B., Ed.; Springer-Verlag: New York, 2004.
13. Xu, L.; Lio, A.; Hu, J.; Ogletree, D. F.; Salmeron, M. *Journal of Physical Chemistry B* **1998**, *102*, 540.
14. Xiao, X.; Linmao, Q. *Langmuir* **2000**, *16*, 8153.
15. He, M.; Blum, A. S.; Aston, D. E.; Buenviaje, C.; Overney, R. M.; Luginbuhl, R. *Journal of Chemical Physics* **2001**, *114*, 1355.