



Supporting Online Material for

Nanoscale Friction Varied by Isotopic Shifting of Surface Vibrational Frequencies

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SUPPORTING ONLINE MATERIAL

Experimental Methods

Three separate atomic force microscopy (AFM) experiments were performed: two using C(001) (one in dry nitrogen, the other in ultra-high vacuum (UHV)) and one using Si(111) single crystal surfaces in dry nitrogen. Prior to all experiments, organic contaminants were removed from both crystals' surfaces by piranha solution (4:1 = $\text{H}_2\text{O}_2:\text{H}_2\text{SO}_4$ at 100°C). The diamond surfaces were H- or D-terminated by an established hot filament process. The acid-cleaned single crystal diamond surfaces were H(D)-terminated by a 1300°C tungsten hot filament at a sample temperature of $\sim 600^\circ\text{C}$ (*I*). The filament was pretreated in methane and the chamber pre-cleaned by atomic H(D) prior to sample termination; the samples were kept far below the filament during ignition, brought close to the filament to reach the target temperature and expose to atomic H(D), then moved away from the filament to ramp down the sample temperature prior to shutting off the filament (*i.e.*, while atomic H was still present). The filament on-time was ~ 20 - 25 minutes, ~ 5 - 10 minutes of which the sample was at its closest proximity to the filament.

The friction measurements on C(001) single crystals were performed in a $< 5\%$ relative humidity (RH) dry nitrogen environment, and in UHV (both with a RHK UHV-300 AFM system). Two crystals, one H-terminated, the other D-terminated, were placed side-by-side in the AFM to facilitate alternating between samples. For both of these experiments, the same amorphous carbon-coated tip (2-4) of radius 46 ± 5 nm (measured by transmission electron microscopy (TEM)) was used. For the UHV measurements, the

two diamond crystals were annealed in vacuum for 2-3 hours at ~ 500 °C (measured by type K thermocouple at the surface), which removes adsorbed contaminants but not the H or D monolayer.

The silicon surfaces were terminated by a process analogous to hydrofluoric acid etching but designed to permit a more controlled isotopic substitution by using potassium fluoride (5). Friction measurements on Si(111) were performed in the dry nitrogen environment only, using a Digital Instruments Multimode AFM with Nanoscope IV electronics (user-modified for force setpoint modulation (6)). Due to the instability of H or D on silicon in air, the terminated silicon samples were mounted in the environmentally-controlled AFM within a few minutes after each H or D monolayer preparation was complete. The silicon nitride AFM tip (Olympus OMCL-RC) had a radius of 35 ± 5 nm, estimated by imaging sharp features on a calibration grating (7). For all experiments, the scan direction was held constant with the tip sliding nominally along the [010] direction on C(001) and the [110] direction on Si(111) (8). Force constants and calibration factors were determined according to established experimental methods (9-11). All experiments were carried out at room temperature. Atomically flat regions of the diamond and silicon samples were identified by AFM topographic images and subsequently used for all friction measurements.

Water droplet contact angles of $>90^\circ$ were observed on freshly processed samples. Si-H and Si-D specimens prepared in identical manners as those used in the AFM experiments were examined by x-ray photoelectron spectroscopy and found to be free of contaminants. Moreover, higher friction (by a multiplicative factor of more than 3 times) was seen on control silicon samples with native oxide.

In contrast with silicon, hydrogenated diamond surfaces are stable in air, permitting longer time-scale spectroscopic measurements to be performed prior to friction experiments. The two diamond samples (one H- and the other D-terminated) were stored in a sealed nitrogen-flushed vial and sum frequency generation (SFG) spectroscopy measurements were then conducted within 24 hours (12). SFG identifies the chemical composition and orientation of surface or interfacial adsorbates through their vibrational spectra (13-17), and is an effective probe of diamond surfaces (18-20). Speciation and coverage are determined by the vibrational frequency of the C-H(D) stretch, and the orientation of the C-H(D) bonds at the interface are deduced by performing polarization null angle analysis (17).

The SFG spectra were taken using s-polarized sum frequency, s-polarized visible, and p-polarized infrared (ssp) light. The surfaces were relatively free of defects and contaminants, as evidenced by the absence of significant dihydride (CH_2) and trihydride (CH_3) peaks and the polarization-dependent SFG spectra (21). The nonzero background and the high energy tail was attributed to the electronic response of the Type Ib substrate (22). The C-D peak is broadened in part due to the coupling of bending vibrations with surface phonons (23).

Friction analysis

The contact mechanics of a paraboloidal tip in adhesive contact with a flat elastic surface is described by a range of behavior that spans from the Johnson-Kendall-Roberts (JKR) model (24) (for large tips and compliant materials with strong, short range adhesion) to the Derjaguin-Müller-Toporov (DMT) model (25) (for small tips and stiff

materials with weak, long-range adhesion), with these limits and the intermediate cases described by the model of Maugis (26, 27). Carpick, Ogletree, and Salmeron (COS) (28, 29) provided an approximate general equation for easily fitting the contact area A to Maugis' parametric solution. A is directly proportional to $K^{2/3}$, where the combined elastic modulus is $K = (4/3) \left[(1 - \nu_{surf}^2) / E_{surf} + (1 - \nu_{tip}^2) / E_{tip} \right]^{-1}$, with E and ν the Young's modulus and Poisson's ratio, respectively, of the surface and tip as indicated.

Without specifying K (since the tip elastic properties are unknown), we simply calculate the effective shear strength, which is proportional to the absolute shear strength as explained elsewhere (30):

$$\tilde{C} = \pi \frac{\tau_o}{K^{2/3}}, \quad (\text{S.1})$$

Representative friction data presented here were selected for their correspondence with the mean value of the effective shear strength associated with the given surface, but the full statistics and uncertainties are evaluated and reported in Table I. To illustrate the high quality of the fits and the error within a given friction measurement at each load, specific examples of friction *vs.* load data for C(001) in UHV with the COS fits are presented in Figure S1. A TEM image of the hydrocarbon-coated tip appears in the inset.

For the experiments on diamond, friction and adhesion depended upon the environment (Table I). The adhesive pull-off force was reduced by 64-87% in UHV, consistent with a compositional change of interfacial materials (*i.e.*, removal of molecular contaminants). Friction forces were lower in UHV overall by a factor of ~ 5 , but the friction contrast between H- and D-terminated surfaces persisted, *i.e.*, τ_o was $\sim 26\%$ greater for the C-H surface independent of the environment and the magnitude of friction

force. Using the UHV environment and annealing the samples removes adsorbed contaminants, which may cause a diminished electronic contribution to friction (discussed further below), a reduction of the interfacial energy, and/or a reduction of the interfacial corrugation (31). Despite the drop in friction forces in UHV, the constant τ_H/τ_D ratio indicates that all contributions to nanoscale friction, whether they are phononic, electronic, or otherwise, may be mediated by a common, fundamental process: the transfer of energy from tip to sample at a rate determined by the vibration of surface atoms. We consider the possibility of an electronic contribution from adsorbates in the discussion below.

Note that for the comparison to the adsorbate damping theory, we deliberately use the same damping constant for Eqs. (2) through (4), because we hypothesize that the two will be directly related, if not identical. As well, we have only considered vibration modes perpendicular to the surface. Vibration modes parallel to the surface also exist. Although the bond stiffness is affected by lateral interactions, the frequency scaling with mass holds.

The adsorbate damping theory in Eqs. (2) through (4) assumes that the individual adsorbates are uncoupled. Persson and co-workers have also considered the case of an infinite coupled monolayer vibrating in its low frequency collective modes, where the damping constant, η , varies as $m\omega^2$ (32). To first order, this yields no dependence of friction upon mass. Our experiment involves a finite number of atoms, which is intermediate to the independent adsorbate case ($\sim m^{-1}$ dependence) and the infinite monolayer case ($\sim m^0$ dependence). Furthermore, defects will tend to localize the sites for energy dissipation. Thus, we may expect some degree of mass dependence within this

simple framework. Our observation of reduced friction for heavier adsorbate mass is therefore consistent with the adsorbate damping model.

The estimated shear strengths (Table I) were calculated using known values for the elastic properties of diamond (36, 37), silicon, silicon nitride, and an estimated modulus (100 GPa) and Poisson's ratio (0.3) for the hydrocarbon-coated tip. Furthermore, we can use our values for τ_o with Eqs. (2) and (3) to make a rough estimate of the dynamical effective mass of the tip, m_{tip} . Assuming that the hydrocarbon film coating the tip is comparable to diamond-like carbon (i.e., $\rho = 2000 \text{ kg/m}^3$ (38), and $c_T \approx 4 \text{ km/s}$), and using measured values for the natural frequency of C-H and C-D on the C(001) surface (39), we calculate the damping constants to be $\eta_H \approx 1700 \text{ THz}$ and $\eta_D \approx 1075 \text{ THz}$. These values are large in comparison with the vibration frequencies of the adsorbates, but cannot be further understood without more specific modeling of the experiment. Regardless, this justifies focusing on the tip as the primary location for dissipated energy, because the damping constants for dissipation within the diamond crystal are much smaller: $\eta_H \approx 11 \text{ THz}$ and $\eta_D \approx 7 \text{ THz}$.

To calculate m_{tip} , we use the surface atom density on diamond (001), $\sigma = 1.6 \times 10^{15} \text{ cm}^{-2}$. While the scanning velocity is $1.2 \text{ } \mu\text{m/s}$, the instantaneous velocity during slip events may be much higher. Though the atomic lattice was not resolved in these experiments, the friction traces consisted of irregular stick-slip events, indicating that the tip apex approaches instantaneous velocities that are much higher than the nominal scan velocity. The maximum possible velocity is given by the tip height ($\sim 15 \text{ } \mu\text{m}$ as measured by TEM) multiplied by the torsional resonance frequency out of contact (271.1 kHz). We neglect the load-dependence of this frequency (40), as we are focused on order-of-

magnitude estimates. This gives an estimated maximum velocity of ~ 4 m/s. Thus, the effective tip mass ranges from $m_{\text{tip}} = 2 \times 10^{-27}$ kg to $m_{\text{tip}} = 8 \times 10^{-21}$ kg for high and low tip velocities, respectively. These values correspond to a single atom for the high velocity case and up to $\sim 10^6$ atoms (a radius of ~ 10 nm) in the low velocity limit (41). These correspond to physically reasonable length scales, given that the contact radius is in the range of a few nanometers.

Additional comments

We present work of adhesion data calculated from the friction vs. load measurements (instead of force vs. displacement curves from purely normal loading), because they were either similar to (for Si) or greater than (diamond) the values measured from force vs. displacement curves (also recorded throughout the experiments). The latter measurements were used to control for changes in the tip over time and for early pull-off, which can often occur in nanoscale friction experiments. We observed no evidence of early pull-off. Hence, while force-displacement data are valuable in these respects, the work of adhesion as calculated from contact area fits to friction vs. load curves yields a more accurate measurement of the instantaneous properties of the contact.

The hydrogenated (or deuterated) diamond surface is insulating, but it conducts in the presence of physisorbed molecules that act as acceptors (42). This surface transfer doping mechanism is diminished due to desorption of physisorbed material by vacuum annealing. As a result, carriers that would otherwise absorb kinetic energy from the tip during sliding are no longer present. Comparing the measurements on H- and D-

terminated diamond performed in air with those performed in UHV allows us to explore this effect in relation to the vibrational contribution (31).

If we assume that the increased friction in dry nitrogen is entirely due to electronic friction via the electrical conductivity endowed by ambient hydrocarbon adsorbates, the damping constant η in the total friction force ($F_{f,vib} = m_{tip} \eta v \sigma A$) may be written as:

$\eta = \eta_{vib} (k_{ph} + k_{el})$, where the constants, k_{ph} and k_{el} , represent the fraction of the total energy that is lost to phonons and electrons, respectively. Thus, if vibrational properties alone determine the dissipation rate, and if k_{ph} and k_{el} are identical for H- and D-terminated surfaces, the ratio of shear strengths will always yield the relation

$\tau_H / \tau_D = \eta_{vibH} / \eta_{vibD} = \text{constant}$. For the diamond experiments presented here, the large drop in friction forces in vacuum suggests that k_{el} may be at least 4 times k_{ph} , if the drop in friction is attributable to the elimination of surface transfer doping.

Figure S1. Individual friction *vs.* load measurements of C(001)-H (red) and C(001)-D (blue) in UHV. The error bars are obtained from the percent error in the (effective) shear strength (~5% for both H and D). Also included are the COS transition fits, where $\alpha = 0.98$, and the pull-off force is set according to the measured pull-off force during the friction measurement. Inset: TEM image of the hydrocarbon-coated tip, with measurement of its radius. Possible changes in tip shape showed no trend, as determined by normal force *vs.* displacement measurements performed throughout the experiments.

References for Supporting Online Material:

1. B. van Zyl, M. W. Gealy, *Rev. Sci. Instrum.* **57**, 359 (1986).
2. U. D. Schwarz, O. Zworner, P. Koster, R. Wiesendanger, *J. Vac. Sci. Technol. B* **15**, 1527 (1997).
3. W. Ding *et al.*, *J. Appl. Phys.* **98**, 014905 (2005).
4. G. Gao, R. J. Cannara, R. W. Carpick, J. A. Harrison, *Langmuir* **23**, 5394 (2007).
5. H. Luo, C. E. D. Chidsey, *Appl. Phys. Lett.* **72**, 477 (1998).
6. M. J. Brukman, G. O. Marco, T. D. Dunbar, L. D. Boardman, R. W. Carpick, *Langmuir* **22**, 3988 (2006).
7. Mikrosmach TGG01 (Tallinn, Estonia).
8. Thermal drift and piezo nonlinearity restrict the directional accuracy to an estimated $\pm 10^\circ$ from the intended scanning direction; this uncertainty is systematic for the diamond single crystals which were co-aligned and therefore does not account for the differences observed between the H and D surfaces.
9. D. F. Ogletree, R. W. Carpick, M. Salmeron, *Rev. Sci. Instrum.* **67**, 3298 (1996).
10. J. E. Sader, *Rev. Sci. Instrum.* **70**, 3967 (1999).
11. C. P. Green *et al.*, *Rev. Sci. Instrum.* **75**, 1988 (2004).
12. S. Baldelli, *J. Phys. Chem. B* **107**, 6148 (2003).
13. D. C. Duffy, P. B. Davies, A. M. Creeth, *Langmuir* **11**, 2931 (1995).
14. M. Buck, M. Himmelhaus, *J. Vac. Sci. Technol. A* **19**, 2717 (2001).
15. J. Y. Huang, Y. R. Shen, in *Laser Spectroscopy and Photochemistry on Metal Surfaces* H. L. Dai, W. Ho, Eds. (World Scientific, Singapore, 1995).

16. M. J. Shultz, C. Schnitzer, D. Simonelli, S. Baldelli, *Int. Rev. Phys. Chem.* **19**, 123 (2000).
17. H. F. Wang, W. Gan, R. Lu, Y. Rao, B. H. Wu, *Int. Rev. Phys. Chem.* **24**, 191 (2005).
18. C. D. Bain, *J. Chem. Soc. Faraday Trans.* **91**, 1281 (1995).
19. C. D. Bain, P. B. Davies, T. H. Ong, R. N. Ward, *Langmuir* **7**, 1563 (1991).
20. P. Guyot-Sionnest, P. Dumas, Y. J. Chabal, *J. Electron Spec. Rel. Phen.* **54/55**, 27 (1990).
21. L. V. Zhirgilei, D. Srivastava, B. J. Garrison, *Surf. Sci.* **374**, 333 (1997).
22. R. P. Chin *et al.*, *Phys. Rev. B.* **45**, 1522 (1992).
23. R. P. Chin, J. Y. Huang, Y. R. Shen, T. J. Chuang, H. Seki, *Phys. Rev. B* **52**, 5985 (1995).
24. K. L. Johnson, K. Kendall, A. D. Roberts, *Proc. Roy. Soc. London A* **324**, 301 (1971).
25. B. V. Derjaguin, V. M. Muller, Y. P. Toporov, *J. Colloid Interface Sci.* **53**, 314 (Nov. 1975, 1975).
26. D. Maugis, *J. Colloid Interf. Sci.* **150**, 243 (1992).
27. D. S. Grierson, E. E. Flater, R. W. Carpick, *J. Adh. Sci. Tech.* **19**, 291 (2005).
28. R. W. Carpick, D. F. Ogletree, M. Salmeron, *J. Colloid Interf. Sci.* **211**, 395 (1999).
29. U. D. Schwarz, *J. Colloid Interf. Sci.* **261**, 99 (2003).
30. U. D. Schwarz, O. Zworner, P. Koster, R. Wiesendanger, *Phys. Rev. B* **56**, 6987 (1997).

31. H. Gang, M. H. Muser, M. O. Robbins, *Science* **284**, 1650 (1999).
32. B. N. J. Persson, E. Tosatti, D. Fuhrmann, G. Witte, C. Woll, *Phys. Rev. B* **59**, 11777 (1999).
33. Y. Sang, M. Dube, M. Grant, *Phys. Rev. Lett.* **87**, 174301 (2001).
34. M. R. Sørensen, K. W. Jacobsen, P. Stoltze, *Phys. Rev. B* **53**, 2101 (1996).
35. G. A. Tomlinson, *Philosophical Magazine* **7**, 905 (1929).
36. E. S. Zouboulis, Grimsditch, M., Ramdas, A.K., and Rodriguez, S., *Phys. Rev. B* **57**, 2889 (1998).
37. J. Turley, G. Sines, *J. Phys. D: Appl. Phys.* **4**, 264 (1971).
38. Y. Oka, M. Kirinuki, T. Suzuki, M. Yatsuzuka, K. Yatsui, *Nuc. Instrum. Meth. Phys. Res. B* **242**, 335 (2006).
39. S. Thachepan *et al.*, *Phys. Rev. B Rap. Comm.* **68**, 041401(R) (2003).
40. S. Maier *et al.*, *Phys. Rev. B* **72**, 245418 (2005).
41. The substrate (tip) volume which is affected by the displacement field generated in the collision corresponds to some tens of atoms--much less than the effective mass of the tip-cantilever system (in the high slip velocity limit).
42. J. Ristein, *J. Phys. D: Appl. Phys.* **39**, R71 (2006).

