Tribological Response Of Silicon Oxide-Containing Hydrogenated Amorphous Carbon, Probed Across Lengthscales

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Abstract
This work examines the structure and properties of silicon-oxide containing hydrogenated amorphous carbon (a-C:H:Si:O) thin films, and how the structure and properties are responsible for the fundamental tribological response of the material. The films are studied through a range of spectroscopic techniques, focused on the surface-sensitive X-ray photoelectron and near-edge X-ray absorption fine structure spectroscopies. The tribological response is studied at several lengthscales: using macroscale ball-on-flat tribometry, at the nanoscale with sharp diamond-like carbon-coated AFM probes, and at the microscale with steel colloids affixed to AFM cantilevers. The spectroscopic study reveals that the films contain a high fraction of SiOx which leads to a structure rich in sp3 carbon-carbon bonding that affords strong protection against oxidative attack at the elevated temperatures in aerobic environments, which is important for demanding applications. At the macroscale, low friction coefficients are achieved upon the formation of an inherently lubricious, soft and polymeric tribofilm whose composition and structure depends heavily on the sliding environment, while the lubriciousness of the resulting tribofilm does not depend on the environment in which it was formed. Nanoscale experiments demonstrate that the shear strength of a sharp, single asperity contact sliding on a-C:H:Si:O is at least an order of magnitude higher than those estimated from macroscale sliding, raising questions about whether the surface passivation theory of DLC lubricity is sufficient to explain macroscale lubricity. Colloidal AFM experiments show, in situ, that low friction is achieved with the growth of the tribofilm via a combination of reduced adhesion and a precipitous drop in the shear strength, which offset a simultaneous increase in the real area of contact. The compilation of results suggests a model of lubrication which relies on both surface passivation of the counterfaces and the soft and viscoelastic properties of the tribofilm, which reduce the effect on friction of nanoasperity pinning.

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TRIBOLOGICAL RESPONSE OF SILICON OXIDE-CONTAINING HYDROGENATED AMORPHOUS CARBON, PROBED ACROSS LENGTHScales

J. Brandon Mcclimon

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ABSTRACT

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J. Brandon McClimon
Robert W. Carpick

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TABLE OF CONTENTS

ACKNOWLEDGMENT ........................................................................................................... II

LIST OF TABLES .................................................................................................................... IX

LIST OF FIGURES .................................................................................................................. X

CHAPTER 1: INTRODUCTION .............................................................................................. 1
Structure and Properties of DLCs .......................................................................................... 1
Tribological Response of DLC’s ............................................................................................ 5
Doping of DLC’s ...................................................................................................................... 8
Fundamental Mechanisms of DLC Lubrication ...................................................................... 9
Applications of DLC’s .......................................................................................................... 13
Development of silicon-oxide doped hydrogenated amorphous carbon (a-C:H:Si:O) .............. 15
References .............................................................................................................................. 17

CHAPTER 2: STRUCTURE AND THERMAL STABILITY OF PIIID-GROWN A-C:H:SI:O ..................................................................................................................... 28
Introduction ........................................................................................................................... 28
Experimental Methods ........................................................................................................... 30
PIIID Film Deposition .............................................................................................................. 30
Humidity Effects .................................................................................................................. 110
Other Materials .................................................................................................................. 113
Endurance Testing ............................................................................................................... 115
Detailed Tip Dynamics ........................................................................................................ 117

Discussion .......................................................................................................................... 122

Conclusions ......................................................................................................................... 127

References ............................................................................................................................ 128

CHAPTER 5 – MICROSCALE TRIBOLOGICAL RESPONSE ............................................. 133

Introduction .......................................................................................................................... 133

Experimental Methodology ............................................................................................... 134

Results ................................................................................................................................ 135

Discussion ............................................................................................................................ 143

Conclusions .......................................................................................................................... 146

References ............................................................................................................................ 146

CHAPTER 6 – CONCLUSIONS AND FUTURE WORK .................................................. 149

References ............................................................................................................................ 153

APPENDIX – SCANNING PROBE METHOD FOR ACCURATE MEASUREMENT AND
MAPPING OF ATOMIC LATTICE CONSTANTS VIA ATOMIC STICK SLIP
DEMONSTRATED WITH MEASUREMENT OF THERMAL LATTICE STRAIN IN CVD
MOS₂ ..................................................................................................................................... 154

Introduction .......................................................................................................................... 154
Experimental Methods................................................................................................................. 155

Results ........................................................................................................................................ 156
  Scan Piezo Lateral Calibration ................................................................................................. 161
  Drift Correction ...................................................................................................................... 163
  Lattice Constant Measurement on Square Lattices ................................................................. 165
  Single Point Lattice Strain Measurement ............................................................................ 167
  .............................................................................................................................................. 169
  2D Lattice Constant Mapping ............................................................................................... 170
  Extension to Piezo Sin Oscillation ...................................................................................... 174

Discussion ................................................................................................................................ 177

Conclusions ............................................................................................................................... 178

References .................................................................................................................................. 178

Igor Implementation Code ........................................................................................................ 181

Sin wave oscillation ................................................................................................................ 193
LIST OF TABLES

Table 3.1................................................................................................................................. 81

Table 4.1: Parameters calculated from published simulation results involving an a-C:H or hydrogen terminated amorphous carbon (h-DLC) sliding against itself, diamond, or hydrogen terminated diamond (h-diamond), where the simulations have been performed with molecular dynamics (MD) or tight-binding quantum chemical molecular dynamics (TB-QCMD). .......... 124
LIST OF FIGURES

Figure 1.1: Ternary “phase diagram” of amorphous carbons as a function of the hydrogen fraction and carbon bonding hybridization. Adapted from Ref. 7......................................................2

Figure 1.2: Trends in Youngs modulus and density as a function of sp³ fraction for various undoped and hydrogen-doped diamond like carbons. Adapted from Ref. 24...............................4

Figure 1.3: Dependence of steady state friction coefficient on the total pressure of water vapor for a ta-C (open diamonds) and a-C:H (filled squares). Adapted from Ref. 38.........................6

Figure 1.4: Effect of gas partial pressure leaked from UHV on the friction coefficient of self-mated a-C:H against a 4 mm ball at 21 mm/s. Adapted from Ref. 46........................................13

Figure 1.5: Selection of automotive engine components now commercially available with DLC coatings. Adapted from Ref. 67 ..................................................................................................15

Figure 1.6: Schematic representation of PIIIID deposition technique used to produce a-C:H:Si:O films..........................................................................................................................16

Figure 2.1. (a) AFM contact-mode topographic images of PIIIID-grown a-C:H:Si:O films before and after annealing at 450°C under aerobic conditions (31±3% RH in air) or in high vacuum (HV) for 1 hour; (b) TEM images of an atomic force microscope (AFM) probe coated with a-C:H:Si:O (PIIID-grown; thickness: 15 nm)...................................................36

Figure 2.2. (a-b) High-resolution Si 2p XPS spectra of PECVD- and PIIIID-grown a-C:H:Si:O acquired before and after annealing at 450°C under aerobic conditions (RH=31±3%) or in high vacuum (HV). Colored lines are curve fits; (c) apparent composition (calculated from XPS data, i.e., without accounting for hydrogen) of PIIIID- and PECVD-grown a-C:H:Si:O before and after annealing at 450°C under aerobic conditions (RH=31±3%) or in high vacuum. .......................37

Figure 2.3. (a,c) C 1s NEXAFS spectra of PECVD- and PIIIID-grown a-C:H:Si:O acquired before and after annealing at 450°C under aerobic conditions (RH=31±3%) or in high vacuum (HV). The C 1s spectra of reference samples (i.e., HOPG and UNCD) are also displayed (dashed lines) for comparison (they represent the two extremes of sp² and sp³ bonding, respectively); (b,d) zoomed view of the absorption edge region of the C 1s NEXAFS spectra. Spectra are pre- and post-edge normalized. ..........................................................................................40

Figure 2.4: Summary of NEXAFS-measured sp³ fractions for the PECVD and PIIIID a-C:H:Si:O films under different annealing treatments.................................................................42
Figure 3.1: a) Representative ball on flat tribometry results for different sliding environments utilizing a hardened steel ball and PIII-D-grown a-C:H:Si:O film on Si(100) substrate. b) Width of a-C:H:Si:O wear track, as measured by calibrated optical microscope, as a function of the number of sliding cycles. Error bars show the spread of data where multiple wear tracks were measured.

Figure 3.2: a) Ball on flat tribometry results for a-C:H:Si:O film after 60 min, 350°C annealing in air. b) Optical microscope image of wear tracks made in laboratory air and surrounding a-C:H:Si:O film. Gray regions are exposed Si substrate. c) Optical microscope images of steel balls upon completion of the tribometer tests. These images show differences between transfer film for a case where the friction remained low throughout the test (Run 1) vs. a case where low friction was lost (Run 5). d) Triboscopy image of the evolution of the friction coefficient as a function of both cycle number and wear track position during Run 2.

Figure 3.3: Wear tracks produced during blowing N₂ tribometer tests of 350°C 1hr. air annealed PIII-D a-C:H:Si:O. Material has been transferred from the 52100 steel ball to the bare Si in the wear tracks.

Figure 3.4: a) Results of three tribometer tests sliding ¼" diameter 52100 steel balls at 3 mm/s on 3 mm track with 0.1 N normal load. Schematics of contact geometry are included in legend for clarity. The steel + tribofilm test was performed with the same steel ball as the steel on a-C:H:Si:O test. The steel on Si test was performed with a new steel ball. b) Single cycle traces of lateral force/normal load for the steel + tribofilm test showing the evolution of friction force and its dependence on track position. For reference, black lines show the lateral forces present for the steel on a-C:H:Si:O test after steady state was achieved.

Figure 3.5: Friction vs. cycle number for tribometer test with intermittent blowing N₂. Vertical dotted lines indicate when N₂ blowing started or stopped. The horizontal dotted lines indicate the steady state friction measured during separate tests in ambient air (red) and blowing N₂ (blue).

Figure 3.6: a) and b) AFM topographic images of tribofilms formed during 500 sliding cycles in blowing N₂ and 50 cycles in air, respectively. The yellow line in (a) shows the approximate position of the TEM cross section shown in Figure 3.17. c) and d) Profiles of the linescans shown in (a) and (b), respectively.
Figure 3.7: AM-AFM image (a) and linescan (b) of tribofilm produced after 100 sliding cycles in ambient air. White light interferometry image (c), linescan (d), and camera image (e) of the same tribofilm produced by the Zygo NewView 6300 interferometer. ........................................... 61

Figure 3.8: a) Example of substantial unload-reload hysteresis frequently observed for quasistatic tribofilm indentation measurements. b) and c) AFM images (with same vertical scale) and linescans for nanoindents of the same tribofilm produced in lab air <12 hours after the indents were produced (green) and 27 days later (red)........................................................... 63

Figure 3.9: Continuous stiffness indentation measurements using a cube corner tip with 220 Hz oscillation frequency of transfer films produced in three environments for different numbers of sliding cycles. For reference, literature indentation measurements for glassy carbon (black star) and polycrystalline graphite (black cross) are presented in (a). ................................................................. 64

Figure 3.10: Measured storage and loss moduli for two environments determined using a Berkovich tip in the CSM mode with a 220 Hz modulation. Data is presented in log-log (a) and log-linear (b) formats. ............................................................................................................ 67

Figure 3.11: Viscoelastic loss tangent determined using 220Hz CSM mode indents with a Berkovich tip into transfer films produced by 100 sliding cycles in lab air or 50 cycles in blowing dry air. ....................................................................................................................... 68

Figure 3.12: a) and b) Typical load-displacement curve obtained from quasistatic indentation measurements and associated series of reduced modulus and hardness values determined for each partial unload segment of the loading sequence. c) Distribution of apparent hardness measurements determined via nanoindentation for 3 ambient environments using Berkovich tip and quasistatic loading. ............................................................................................................. 69

Figure 3.13: Mechanical properties determined by quasistatic Berkovich nanoindentation for several environments. ................................................................................................................................. 70

Figure 3.14: SEM/EDX mapping of PIIID a-C:H:Si:O transfer films formed in three different environments. Each column is a single tribofilm, with each row showing a different analysis, in order: secondary electron image, EDX of carbon Kα, silicon Kα, and oxygen Kα X-rays. ................. 72

Figure 3.15: 532 nm Raman spectra for the PIIID-grown a-C:H:Si:O and transfer films produced in 3 ambient environments during macroscale tribometer experiments that differed only in the number of cycles performed. ........................................................................................................... 74
Figure 3.16: a: SEM image of tribofilm after deposition of protective Pt pad atop four nanoindentons that were part of a pattern of 12 nanoindentations. b: Tribofilm after partial completion of the cross sectioning process. Residual indentations filled with Pt for two of the indentations remain visible.

Figure 3.17: a-d, top row: HAADF images of four regions where nanoindenters were performed prior to cross sectioning of the tribofilm produced after 500 cycles of sliding in a blowing N₂ environment. a-d, bottom row: EELS composition maps for the same four regions. Si mapping omitted for clarity since O/Si regions fully overlapped e: EELS low loss spectra for carbon-rich areas of each of the four regions. f: Representative carbon K-edge spectra for the tribofilm and an AFM probe coated with the unmodified a-C:H:Si:O.

Figure 3.18: Composition maps for carbon, oxygen, and silicon from spot 1. A high resolution EELS spectrum from the Si-rich portion of the image is included for reference.

Figure 3.19: HAADF (left) and EELS composition map (right) of a Si AFM probe which has been coated with a-C:H:Si:O in a nominally identical deposition to the one used to prepare the flat samples subjected to tribometry.

Figure 3.20: TEM images demonstrating the location of four indentation performed prior to the cross-sectioning process. Red circles indicate the position of high resolution images and associated FFTs in the lower panels.

Figure 4.1: Friction as a function of applied normal load in 50±1% RH air. Each trace was measured by decreasing the load by 0.25 nN after every scan line across a 625x5000 nm² AFM image. The rectangular imaging box was used to prevent overlap of sequential scan lines. Each trial was performed in a randomized order.

Figure 4.2: Topographic image and associated linescan of worn surface of a-C:H:Si:O after sliding a silicon AFM tip at 200 nN applied normal force across 500 nm with slow scan disabled for 256 cycles in 47±1%RH air. A large volume of silicon which has been transferred from the AFM tip to the wear track is observed. The characteristic triangular shape seen in the image is an artifact due to the fact that the tip has been blunted by this material removal, and its remaining triangular-shaped base is obtaining the image.

Figure 4.3: Friction trends at various loads for (a) & (b) ta-C coated and (b) diamond-coated AFM probes for reciprocating sliding across 2.4 µm on previously unworn a-C:H:Si:O. Trials are
numbered chronologically. The horizontal arrow in (a) is a guide to the eye. Every trial was performed on previously unworn a-C:H:Si:O.

Figure 4.4: Bright field TEM imaging of (a) the blunt ta-C coated AFM probe used for the testing in Figure 4.3a after completion of sliding tests and (b) a different, new ta-C coated AFM probe with a smaller apex radius.

Figure 4.5: Friction vs. Load for a ta-C probe sliding on a-C:H:Si:O with progressively decreasing load. The image size was 0.625 \times 5 \, \mu m. Slow scan was disabled for the solid line traces so that successive scan lines were nominally over the same area. Images were acquired in the order presented in the legend.

Figure 4.6: a) Friction image on a-C:H:Si:O in 50\pm1\%RH air with the normal load increased by 0.8 nN after each scan line. In the center of the image is a preworn region produced by repetitively scanning the same line 256 times at 400 nN normal load. b) Average friction across unworn region and linescan through preworn region of the image area. The abrupt change in the worn region friction at 315 nN is due to the worn region not extending across the entire image.

Figure 4.7: Friction (a),(c) and height (b),(d) image and linescans of region in Fig. 4, post-wear, performed at 0 nN applied normal load. Linescans are taken from bottom to top of the images. There is appreciable wear and the friction is high relative to the unworn region. Friction is higher in the worn region due to the non-monotonic change in the shear strength with applied load when sliding in humid air.

Figure 4.8: Tests with single crystal diamond probe (tip radius = 14 nm) sliding on a-C:H:Si:O in 26 \%RH air. (a) Stiffness data and fit from the lateral force lock-in response to a \pm 1.8 nm, 2 kHz modulation in the lateral direction. b) Friction vs. normal load, slow scan disabled, 200nm scan length, 512 scan cycles per image, normal force incremented \pm 0.08 nN per cycle, repeated once (2nd image is hashed trace). c) Shear strength calculated from data in (b). The rainbow color scheme of the traces follows the measurement, with red at tip pull-in, then green, blue, and finally violet at pull-off.

Figure 4.9: Measured interfacial shear strength as a function of normal load for a ta-C coated AFM probe on a-C:H:Si:O in 32\pm1\% RH air with slow scan disabled. The tip radius from BTR was 25 nm during this test. Inset: Friction vs. load used in calculation of interfacial shear strength.
Measurement was performed with increasing load from tip pull-in (red) to tip pull-off (violet).

Figure 4.10: Pulloff force measurements across unworn regions of a-C:H:Si:O in dry or humid N\textsubscript{2} using a single crystal diamond probe. Pulloff force measurements were captured across an 8x8 area grid. Average ± standard deviation values are tabulated in the legend.

Figure 4.11: Shear strength measurements for a ta-C tip sliding on a-C:H:Si:O in alternating dry and humid N\textsubscript{2} environments. (a) Comparison of results with slow scan enabled to results with slow scan disabled i.e. reciprocating sliding. (b) Comparison of reciprocating sliding in subsequent repetitions of the measurement showing a continuous decrease in shear strength due to a progressive tip change.

Figure 4.12: Shear strength determined for a single crystal diamond tip sliding on a-C:H:Si:O in <1 or 50±1 %RH N\textsubscript{2}. A 2 KHz, ±1.8 nm lateral oscillation used for stiffness measurement. Imaging parameters for “reciprocating” scans: 200 nm scan size, 512 cycles, normal force increment ±0.08 nN. Imaging parameters for “imaging” scans: slow scan on, 1x1 μm\textsuperscript{2} scan size, 128 lines, normal force increment -0.34 nN.

Figure 4.13: a) Shear Strength as a function of applied normal load for a ta-C AFM tip sliding on a-C:H in dry or humid N\textsubscript{2}. All measurements performed with slow scan OFF. b) Friction vs. applied load for a ta-C AFM tip sliding on μ-crystalline diamond in two environments. Trials 1 & 2 for each environment were performed immediately sequentially on the same sliding region. The set of trials in each environment were performed sequentially with the same tip but on different areas of the sample.

Figure 4.14: a) Endurance test of reciprocating sliding of ta-C probe on a-C:H:Si:O with an applied load of 20 nN. Inset shows friction response over initial 1000 cycles of sliding. b) Topographic image of sliding region after test in (a) showing blistering of contact region. c) Linescan of blistered region in (b).

Figure 4.15: Comparison of friction force traces for a ta-C probe during reciprocating sliding at 100 nm/s across 100 nm on MoS\textsubscript{2} or a-C:H:Si:O either at the start of a reciprocating wear test or after 128 cycles of sliding.

Figure 4.16: Schematic illustration of surface passivation effect which is a hypothesized mechanism for the nanoscale run-in effect.
Figure 4.17: Illustration of analysis method for counting slips during sliding. The traces were generated by smoothing then taking the time derivative of the data presented in Figure 4.15. The selected threshold value for counting a “slip” is shown as a horizontal purple line.

Figure 4.18: a) Friction and slips per cycle during a reciprocating sliding experiment of a ta-C probe on a-C:H:Si:O with an applied load of 30 nN in <5 %RH N₂. b) Counted slips per cycle as a function of the friction with a linear fit of the data.

Figure 4.19: Results of multibond model simulations performed by Zac Milne. Number of slips is plotted as a function of the input number of bonding sites as well as the average friction.

Figure 4.20: Pearson correlation between friction and counted slips as a function of the selected threshold for both experimental as well as simulation results. The dotted line shows the minimum magnitude of correlation often cited as evidence of a significant correlation.

Figure 5.1: Various signal channels during reciprocating sliding at 4 µm/s across a 2 µm wear track of a steel colloid on a-C:H:Si:O with a 1 µN normal load. A 50 pm, 3 kHz Z-oscillation was applied during the test, which allowed for tracking of the normal stiffness and phase.

Figure 5.2: Friction force as a function of sliding cycles during reciprocating sliding of the steel colloid on a-C:H:Si:O in 50%RH N₂ with a 1 µN load.

Figure 5.3: (a) Topographic contact-mode AFM image of steel colloid prior to reciprocating sliding test. (b) Topographic tapping-mode image of colloid after reciprocating sliding test. Green circles represent nominal contact area determined from DMT contact mechanics. (c) Linescan from (b).

Figure 5.4: Friction vs. applied normal load for a steel colloid sliding on a-C:H:Si:O with or without a tribofilm in multiple environments.

Figure 5.5: Friction vs. load curves for the tribofilm on colloid geometry while sliding on unworn a-C:H:Si:O as a function of the relative humidity in N₂.

Figure 6.1: Normal stress vs. shear strength for a ta-C probe of radius 45 nm during reciprocating sliding on a-C:H:Si:O in multiple environments.

Figure A.1: (a) Image FFT of the lateral force channel of a 2D lattice-resolved contact-mode AFM image of bulk MoS₂ and (b) a single linescan spanning the X* axis of the same image. The linescan shows that intensity associated with all diffraction spots is present.
Figure A.2: Schematic representation of the measured quantities $X_1$, $X_2$, $X_3$ in 2D reciprocal space for a hexagonal lattice such as graphite or MoS$_2$. A mirror symmetry exists for the measurement across the scan direction axis. ................................................................. 159

Figure A.3: a) Example force traces while sliding an AFM probe on natural MoS$_2$ b) Schematic representation of the normal force slips on the atomic lattice measured in (a). ......................... 160

Figure A.4: Comparison of FFTs from 50x50 nm$^2$, 1024x1024 pixel$^2$ image computed in 2 different ways: averaging FFTs from the 1024 individual scanlines or combining all data into a single 1D line prior to FFT. The data brackets a single atomic stick-slip peak. ....................... 161

Figure A.5: Calibration data for the AFM fast scan direction in an RHK350 AFM with R9 controller in dry N$_2$ conditions. Data is used to calculate the apparent lattice constant on an MoS$_2$ sample at a given maximum piezo voltage during the scan. The piezo calibration constant used was 30.785 nm/V. Red data points are from calibration using a 2D image FFT on bulk MoS$_2$ for maximum scan piezo voltages <20 V (<500 nm), and using a TGZ1 calibration grating (NT-MDT, Moscow, Russia) for the scans longer than 3 µm. Blue data points come from using the linescan FFT technique discussed in the manuscript, also on bulk MoS$_2$. Error bars are the standard deviation of data acquired at scan frequencies between 0.5 and 5 Hz. The solid line is a quadratic fit to the linescan calibration data. ................................................................. 163

Figure A.6: a) Lattice resolved contact mode AFM image on NaCl(001) surface. b) FFT of time-resolved lateral and normal force traces. Peaks due to stick-slip periodicity are annotated as $f_1$ and $f_2$. It was often the case that stick-slip periodicities could be resolved in both force channels. ........................................................................................................................................ 166

Figure A.7: Lattice constants measured on bulk and CVD-grown monolayer MoS$_2$ by continuous scanning at 500 nm/s across a 50 nm scan length. Data are shown in the order in which they were acquired. After 20 min of scanning to stabilize the piezo trajectory, force data was acquired at 97.7 kHz for 5.369 s and an FFT performed. Twenty sequential FFTs were averaged within the AFM software to create a spectrum for analysis. Error bars are the standard deviation of the lattice constant calculated from at least 5 spectra. The calibration constant of the microscope was adjusted to ensure the first measurement on bulk MoS$_2$ was centered at the literature value 0.3161 nm. ................................................................................................................................... 167
Figure A.8: Topographic and friction images of regions on CVD MoS$_2$ where the lattice strain was measured in Figure A.7: (a)-(b) spot 1, (c)-(d) spot 2, (e)-(f) spot 3. Spots 1 and 2 were taken on different regions of the same flake. Spot 3 was taken near the center of a much larger flake. The 3-pointed star polygons in (e) are regions where a second layer of MoS$_2$ has grown atop the ML MoS$_2$. The lattice strain measurements were acquired from a 50 nm linescan at the center of each region, as illustrated by a light blue line of length 50 nm in the center of (a) with an arrow to guide the eye. ................................. 169

Figure A.9: a) Simulated stick-slip force trace with a periodic phase shift 0.3*2$\pi$ b) FFT of simulated force traces with periodic phase shifts of various amplitudes. In all cases, the resulting spikes are well fit by a Sinc function. ................................................................. 171

Figure A.10: a) Example fitting of the lateral force FFT to determine the stick-slip frequency for three sequential subregions of a 100x100 nm$^2$ image of HOPG which has been subdivided into 8x8 equal regions. b) Map of the lattice constants determined for the HOPG image in (a). Each subregion is 12.5 nm square c) The same data as in (b). The green envelope is the standard deviation of the data. The red envelope is the absolute error of the measurement determined by repeating the measurement 4 times. The dotted line is at the true lattice constant for HOPG. .......................................................................................................................... 173

Figure A.11: a) FFT of simulated force trace generated from listed equation which simulates a 5 nm, 50 Hz sin oscillation on a material with a lattice periodicity of 3 nm$^{-1}$. b) Experimental FFT of lateral force trace on natural MoS$_2$ while oscillating tip at 50 Hz with amplitude calculated to be 23nm. $f_1$ is identified on the basis of lattice symmetry. c) Calibration curves for sin oscillation technique at 50 and 500 Hz. Estimates of the amplitude based on counting slips for 50, 500, 5000 Hz are included for reference. Data are fit with quadratic functions................................. 176
CHAPTER 1: Introduction

The silicon oxide-containing hydrogenated amorphous carbon (a-C:H:Si:O) studied here exists under the broad category of diamond-like carbon (DLC), and more specifically, under the sub-category of amorphous hydrogenated carbon (a-C:H). DLC’s are a class of materials whose name derives from the fact that they possess mechanical properties similar to diamond, which is exceptionally hard and stiff. DLC’s are amorphous, possessing no long-range order in the arrangement of their constituent atoms. a-C:H’s are the most technologically successful of the DLC’s, owing primarily to the fact that they can be deposited to substantial thicknesses on a variety of substrates thanks to their low temperature synthesis.

Structure and Properties of DLCs

The amorphous nature of DLCs creates difficulty in the description of their structure, a trait shared with other amorphous materials which are intensively studied at the present time. Whereas crystalline materials can be described within a clear framework comprised of the atomic lattice itself, a number of distinct defect types and their density, along with a microstructure composed of individual grains with distinct orientations, the number of parameters that can be measured and specified for DLCs (and other glasses) is quite limited. As a starting point, which is quite useful for tribology applications specifically, the degree of sp$^3$ hybridization of the carbon in the DLC can be measured and is critical in determining the mechanical properties. Diamond is a fully sp$^3$-hybridized carbon lattice with the highest stiffness in compression and hardness of any natural material. As the sp$^3$ fraction increases, DLCs are endowed with higher modulus and hardness values, rivaling that of diamond for the variants with the highest sp$^3$ fractions. This is critical in controlling the wear rate of a tribological interface. The hydrogen content of a DLC is also an important measurable parameter. Owing to the amorphous structure, hydrogen may be incorporated into DLC in any proportion, and is frequently included intentionally. In a tribological context, this is because increasing the hydrogen fraction increases the lubricity of the DLC in inert environments for reasons that will be discussed later. It also directly reduces the modulus and hardness of the resulting DLC as an undesirable consequence. This occurs because strong sp$^3$ C-C bonds which
resist deformation are replaced with pairs of C-H bonds which do not.\(^6\)

These two parameters and their use in the taxonomy of DLCs is ubiquitously summarized in the ternary “phase diagram” or “Robertson diagram” presented in Figure 1.\(^7\) The various categories of DLC presented in the figure are mere guidelines, but useful ones. The tetrahedral amorphous carbons, doped with hydrogen (ta-C:H) or undoped (ta-C), are characterized by very high hardness and modulus owing to their diamond-like tetrahedral sp\(^3\) C-

![Figure 1.1: Ternary “phase diagram” of amorphous carbons as a function of the hydrogen fraction and carbon bonding hybridization. Adapted from Ref. 7.](image)

C bonding. They are extremely durable and can have desirable properties, tribological and otherwise. Unfortunately, they also generally have a very high degree of internal stress (2-8 GPa in the case of ta-C\(^8\)), which limits the thickness to which they can be deposited without becoming vulnerable to delamination from their substrates. This internal stress can be substantially relieved without compromising the mechanical properties by high temperature (>600°C) annealing,\(^9\)-\(^11\) but then the flexibility in choice of substrate is severely restricted. The amorphous carbons, hydrogen doped (a-C:H) and undoped (a-C) are the most technologically popular variants at the present time, due to their still-impressive mechanical properties and less restrictive substrate selection. The other materials depicted, including glassy carbon and
graphitic carbon, distinguished by their degree of structural disorder, and the hydrocarbon polymers, which have poor mechanical properties due to the much lower degree of C-C interconnectedness, are not considered DLCs. The specific a-C:H:Si:O discussed in this manuscript could be described as a variant of ta-C:H, as will be shown later.

While hydrogen and the carbon hybridization ratio are the most important and often discussed structural parameters, other aspects of the structure can be characterized. Raman spectroscopy and X-ray photoelectron spectroscopy can be used to characterize the distribution of sp²-hybridized carbon within the material. It has been shown that sp² sites in an sp³ C matrix are mobile at elevated temperatures and can diffuse to form sp² clusters, with a modest activation energy required. This process is critical to internal stress relief via post-growth annealing in ta-C, which is necessary to grow adherent films in excess of 1 µm. The clustering of sp² carbon also affects the optical transparency and electrical conductivity of DLC films. Recent attempts have been made to further characterize the nature of sp² clustering in DLC by measuring the relative fractions of clusters composed of either nanocrystalline-graphite, fused aromatic rings, or olefinic chains, though the resulting model has not yet achieved broad acceptance. This model is intended as a further development of the Ferrari 3-phase model, but the ability to achieve similarly accurate predictions about DLC properties and behavior with the Ferrari model and measurement of the hydrogen fraction likely contribute to the meager interest so far.

Other characterization techniques have been applied to learn more about the structure of DLC. Fourier transform infrared (FTIR) spectroscopy is useful in that it can directly probe the bonding environment of the sp³ fraction of the film as well as all C-H bonds, but the results are generally qualitative. Nuclear magnetic resonance (NMR) provides quantitative information about the carbon hybridization ratio as well as the fraction of sp³ or sp² carbon which is hydrogenated, which is useful because unhydrogenated sp³ C-C bonds are directly responsible for the stiff mechanical properties of DLC. NMR can also provide measurements of the degree of bonding disorder (in bond lengths and angles), which has provided important context about the aforementioned investigations into strain relief of as-deposited ta-C with annealing. 
Given the structural parameters discussed so far, many properties of DLC and their dependence on structure are now well-understood. The highest sp³ variant of DLC is ta-C, which can have sp³ fractions approaching 100%. These films are exceptionally stiff and can achieve hardness and elastic modulus values in excess of 80 GPa and 1000 GPa, respectively.\(^\text{10}\) As the sp³ fraction is reduced the mechanical properties become progressively less stiff, with high-sp² sputtered amorphous carbons having hardness and modulus in the range of 10 GPa and 100 GPa, respectively.\(^\text{2}\) Hydrogen can also be added to the films to change their behavior. This comes at the expense of reducing the hardness and modulus for reasons previously discussed. Nevertheless, a-C:H with hardness and modulus as high as 22 GPa and 180 GPa can be attained.\(^\text{23}\)

![Graph showing trends in Young's modulus and density as a function of sp³ fraction.](image)

**Figure 1.2:** Trends in Youngs modulus and density as a function of sp³ fraction for various undoped and hydrogen-doped diamond like carbons. Adapted from Ref. 24.

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\(^\text{10}\) As the sp³ fraction is reduced the mechanical properties become progressively less stiff, with high-sp² sputtered amorphous carbons having hardness and modulus in the range of 10 GPa and 100 GPa, respectively.

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\(^\text{23}\) Nevertheless, a-C:H with hardness and modulus as high as 22 GPa and 180 GPa can be attained.
for modest hydrogen fractions of up to about 30%. Further increases in hydrogen fraction lead to a rapid dropoff in hardness and modulus as well as an increase in the sp³ fraction as the film becomes polymeric. Some of these trends are summarized in Figure 1.2. The modulus trend for the a-C:H variants with density is qualitatively similar to that presented for ta-C.

The electronic and optical properties of DLC’s are primarily controlled by the density and distribution of sp² sites within the matrix. An intuitive way to understand this is to consider the pure crystalline forms of sp² and sp³ matrices: graphite and diamond. Graphite is an opaque conductor whereas diamond is a transparent insulator. DLC’s lie between these two extremes. They typically behave as semiconductors, with a bandgap proportional to the sp³ fraction. The bandgap is locally compressed in the vicinity of sp² clusters, with the reduced local bandgap being primarily due to bond angle disorder rather than graphitic ordering. The degree of clustering within the sp² fraction also modulates the conductivity, with more clustering leading to higher conductivity. The conduction is via hopping between sp² sites/clusters, though the details of the conduction mechanism are still debated. The optical properties are similar to the electrical properties, with higher sp³ associated with higher optical transparency.

**Tribological Response of DLC’s**

The potential of DLC’s for tribological applications was recognized soon after the first surge of research activity on these materials in the early 1970s. Solid lubricants have been employed for many decades in various forms, generally from materials with low modulus and hardness values that correlated directly with the easy shear deformation that leads to low friction coefficients. Examples include MoS₂, graphite, polymers, soft metals such as Au, In and others. The drawback to using such materials was their inevitably poor wear resistance conferred by soft mechanical properties. DLC’s represented something new: extremely hard materials that achieved low friction coefficients nonetheless, even in dry sliding conditions. Crucially, because they were deposited at low temperatures via sputtering or plasma-based processes, they could also be deposited on most substrates, giving them a broad depth of industrial potential.
The friction response of DLC’s under unlubricated conditions is qualitatively universal, with a few caveats. To start with, there is a strong dependence of friction on environmental humidity across the class. In the case of hydrogen free DLC’s, and even other Carbon allotropes like diamond and graphite, friction can be very high in vacuum or dry environments. Once environmental humidity is added, friction coefficients typically drop to <0.2. Conversely, hydrogenated DLC’s (a-C:H, ta-C:H) typically have very low friction coefficients in low-humidity environments, typically below 0.1, with friction coefficients increasing, sometimes to 0.2 or greater, in humid environments. This is schematically illustrated for representative ta-C and a-C:H samples in Figure 1. In the case of some highly hydrogenated DLC’s, friction can be <0.01, a state now commonly referred to as

![Figure 1.3: Dependence of steady state friction coefficient on the total pressure of water vapor for a ta-C (open diamonds) and a-C:H (filled squares). Adapted from Ref. 38.](image-url)
superlubricity, though it should be noted that this term is misleading in that friction forces do not vanish like resistance or viscosity do in the cases of superconductivity or superfluidity. These materials are a subject of intense investigation as an in-depth understanding of the basic mechanisms leading to superlubricity has immense technological potential.

While the basic dependence of friction on humidity holds true universally for DLC’s, the specific friction coefficients achieved can depend on the particular system under study. Non-Ammontonian behavior, where the friction coefficient has a dependence on the load, is commonly reported for DLC contacts. This is usually attributed to the formation of a soft tribofilm which converts the contact geometry from a typical macroscale multi-asperity contact to one that behaves as a single asperity. Such behavior can make comparisons of friction coefficients between studies problematic, even in cases where the sliding environment and film/counterface structure are held nominally the same. In some DLC systems, it has been found that particular counterface structures/chemistries and environments lead to high or fluctuating friction. In these cases, this behavior has been attributed to poor adhesion of a transfer or tribofilm to the counterface. In most DLC systems, it has been noted that a transfer or tribofilm composed of material transferred from the DLC film is necessary for low friction coefficients to be achieved, and hence good adhesion of this film to the counterface is a prerequisite for achieving low friction.

The wear behavior of DLC’s sliding in dry environments can vary quite substantially from system to system, but again there are general trends. Wear rates tend to be extremely low, in some cases producing some of the lowest known wear coefficients for any material. DLC’s with higher moduli and hardness values (again, correlated with higher sp³ and lower hydrogen fractions) experience lower wear rates than less stiff DLC’s under optimized environmental conditions. In the case of hydrogenated films, higher humidity and oxygen levels are correlated with higher wear rates (though not always), which is often attributed to oxygen etching of carbon in the films. The opposite relationship between humidity and wear exists in the case of unhydrogenated DLC’s. The high friction in inert environments leads to very high wear caused by covalent bonding across the sliding interface and results in a high wear rate due to the subsequent breaking of these adhesive junctions. Higher humidity minimizes this
adhesive bonding, and the limited studies of wear as a function of humidity indicate reduced wear with higher humidity, although no systematic study of the wear rate as a function of humidity has ever been done.

**Doping of DLC’s**

While DLC’s offer the ability to modulate a number of properties via the few structural parameters discussed so far, the desire to further tailor and improve properties and behavior has led researchers to dope DLCs with many additional elements.\(^6^7\) Two broad categories of doped films exist: DLCs doped with light elements, and those doped with metals.

Among the light elements, fluorine-doping has been extensively studied and utilized.\(^6^8\)–\(^7^2\) Fluorine doping leads to films with extremely low surface energy, similar to the surface energies achieved in Teflon thanks to the strong, inert C-F bonded structure.\(^7^1\) Similar to doping with hydrogen, doping with fluorine leads to a reduction in network cross-linking, leading to a reduction in modulus and hardness, however, doping up to \(\sim 20\%\) F creates films with durability similar to standard DLC while preserving the reduced surface energy.\(^7^3\) Boron is another element that has been investigated as a DLC dopant, primarily for possible use in electronic applications, motivated by studies showing its effectiveness in controlling surface oxidation.\(^3^0,^7^4\) Nitrogen doped films have also been produced. Nitrogen doping serves to increase the conductivity of the DLC,\(^7^5\) and promising results have been obtained for the use of N-doped DLCs in electrochemical applications.\(^7^5,^7^6\) A combination of reduced internal stress and high hemocompatibility in N-doped DLC has led to consideration of the material as a coating on medical implants.\(^7^7,^7^8\)

Of particular interest to the work presented here are prior studies of oxygen and/or silicon doped DLCs,\(^1^5,^6^9,^7^9–^8^4\) which will be discussed in more depth at the end of this chapter.

In addition to doping with light elements, DLCs have been doped with metals including Cu, Ag, Au, W, Ti, and Mo.\(^6^7\) Doping with Cu, Ag, and Au was performed to improve the conductivity of the resulting DLCs. In particular, Cu-doping has been investigated to improve the conductivity across brushes in direct current motors used in automotive applications.\(^5^5\) It is known that doping with metals, generally leads to a microstructure composed of DLC...
interspersed with nanoscale clusters of the metallic elements, which clearly improves the conductivity of such DLC's. In the case of the studied Cu-doped DLC studied under sliding conditions, a tribofilm was formed which was predominantly composed of Cu which was used to explain the desired high electrical conductivity across the sliding interface. Doping with refractory metals such as W, Ti, and Mo can lead to several improvements in DLC properties: improved adhesion to the substrate, reduced residual stress, and improved electrical conductivity. Such films have garnered substantial technological interest and have been utilized commercially across a number of automobile engine components in recent years. They have also been adopted in semiconductor fabrication where static electricity buildup must be precluded without compromising tribological properties. Nevertheless, a fundamental understanding of how such doping leads to improved tribological properties is still lacking.

**Fundamental Mechanisms of DLC Lubrication**

The mechanisms responsible for the very low friction of DLC's in dry sliding conditions has been investigated for decades in hopes of achieving a sufficient understanding to allow for the rational design of DLC’s with improved tribological response. A number of mechanisms have been hypothesized and several have achieved substantial support in the literature. The most successful of these will be reviewed here.

The most widely accepted theory of solid lubrication of DLCs is referred to as surface passivation. This is based on the hypothesis that friction in DLC tribosystems is dominated by covalent bonding of C atoms at the surface of the DLC with the counterface. Surface passivation occurs when C atoms at the DLC surface are bonded to unreactive functional groups such as C-H or C-OH leading to repulsive interactions with the counterface material. At this point, there is overwhelming support for the importance of this mechanism. Spectroscopic studies have demonstrated an enrichment in C-H and C-OH bonding at the surface of DLC’s in the wear tracks of DLC after tribological testing. In one particular example, an a-C was tribologically tested in an atmosphere of molecular deuterium. After the test, spectroscopic data revealed an enrichment of the wear track surface with deuterium, unequivocally demonstrating that deuterium in the environment had been incorporated into the surface region of the DLC during the testing. Some spectroscopic studies have also demonstrated an
enrichment in environmental species in the wear track with a simultaneous absence of graphitic ordering of the carbon,\textsuperscript{83,86} which shows that graphitization, a competing theory for the lubrication of DLCs, is absent, at least on the DLC side of the interface. Molecular dynamics (MD) simulations of sliding against DLC have also shown directly that DLC surfaces become terminated with passivating species and this passivation reduces bonding across the interface and friction.\textsuperscript{89,91–94} More accurate simulations using density functional theory and ab initio methods have also demonstrated that it is energetically favorable for environmental species to adsorb to carbon surfaces with dangling bonds, and also support the results of MD simulation showing surface passivation occurring to reduce friction in sliding simulations.\textsuperscript{48,68,95–97}

The second important friction reduction mechanism is the formation of lubricious tribofilm on the counterface sliding against a DLC surface. The primary support for this lubricating mechanism is the fact that the presence of a tribofilm is a prerequisite for achieving low friction,\textsuperscript{90,98,99} most clearly demonstrated in cases where adhesion of the tribofilm to the counterface is poor, leading to occasional removal of the tribofilm, which can be directly correlated with sudden, transient increases in the friction coefficient.\textsuperscript{100} Another study demonstrated that etching off the oxide layer of a steel counterface to improve the adhesion of the tribofilm led to more rapid DLC run-in and a lower steady state friction coefficient.\textsuperscript{54} Unfortunately, the mechanism responsible for the lubriciousness of tribofilm remains elusive. A number of researchers have suggested that such tribofilms are graphitic in nature and achieve their lubriciousness via the same mechanism leading to low shear strength in graphite solid lubricants: easy shear between adjacent graphene planes in the graphite. The conclusion that the tribofilms are graphitic is almost universally based on an interpretation of Raman spectroscopy data with the Ferrari model, which is used to analyze as-deposited amorphous carbons and their evolution under annealing.\textsuperscript{4,50,101–103} Implicit in the conclusions that the tribofilms are graphitic is the assumption that the evolution of the tribofilm structure after adhesive transfer from the DLC is equivalent to the evolution of a DLC under thermal annealing. Such conclusions have not been confirmed by additional characterization techniques. In fact, there is some evidence in the literature that DLC tribofilms may possess a polymeric structure. In one case, researchers found spectroscopic evidence that the tribofilm of an a-C:H:Si contained hydrocarbons oriented along the sliding direction.\textsuperscript{99} Some atomic force microscopy
(AFM)-based mechanical characterization suggests the tribofilms are extremely soft. The strongest evidence, however, comes from a very recent TEM investigation of tribofilms grown from a-C:H and a-C:H:Si:O. This study demonstrated that there is a modest enrichment in the sp² fraction of the tribofilm relative to the as-deposited DLC, but not of a magnitude that would suggest the production of significant quantities of graphite. Additionally, no graphite domains were detected via imaging or diffraction in the TEM.

Further investigation of tribofilms has been hampered by some inherent difficulties in their study. One is that tribofilms are in general very thin, generally <100 nm, which makes determination of their mechanical properties very difficult, even with nanoindentation. For another, the volume of a tribofilm is very small. This makes bulk characterization techniques, such as dynamic mechanical analysis (DMA), which is routinely used to characterize the mechanical properties, impossible to employ in their study. An additional difficulty involves simulations. Since little is known about their detailed structure, it is very difficult to construct a reliable tribofilm structure for simulation. Existing methods for producing DLC structures for simulation, such as rapid quenching of a melt or energetic atom deposition, are clearly inappropriate as they will produce DLC structures. Given the extremely limited accessible timespans in MD, ab initio, and DFT methods, a realistic tribofilm cannot be produced by simulating a sliding test of a standard DLC structure. This inability to simulate tribofilms is a major roadblock in the further understanding of tribofilms, and by extension, DLC lubricity. Given the small number of experimentally accessible structural parameters, simulations of DLC behavior in tribological contacts has been crucial to our understanding of the lubricity of DLC structures, and not having similar capabilities for the study of tribofilms is a serious problem.

Additional insights about lubrication mechanisms have been identified, though their importance relative to the well supported mechanisms of surface passivation and tribofilm formation is unclear. In several studies, it has been shown that sp² bonds in worn DLC can be preferentially oriented after sliding in the plane of the film. This has led researchers to suggest that this is important to lubrication for 2 reasons: 1) having C-C bonds in the plane of the film makes it more difficult for the them to be broken to create dangling bonds and subsequent adhesive junctions with the counterface and 2) this arrangement puts the π*
antibonding orbital in the region between the two counterfaces leading to a repulsive interaction with the counterface.

Some researchers have noted an inverse correlation between viscoplasticity and the friction coefficient in inert or vacuum environments.\textsuperscript{5,6,54} Viscoplasticity is a dependence of the measured hardness on the strain rate, with higher values corresponding to a more rapid increase in the measured hardness with increasing strain rate. In the context of DLC’s, it is thought that increased viscoplasticity is correlated with a reduction in the degree of cross-linking of hydrocarbon chains, allowing for easier plastic relaxation. Intuitively, viscoplasticity correlates with increasing hydrogen fraction, which can be rationalized as hydrogen terminating dangling carbon bonds that would otherwise form crosslinks i.e. having a polymeric character. Friction is hypothesized to be reduced by network relaxation under asperities, which would reduce the local normal pressure, minimizing the formation of reactive dangling bonds and aiding in the stabilization of the tribofilm against delamination. At present though, there is no further evidence for such effects beyond the correlation between viscoplasticity and the friction coefficient.

As mentioned earlier, an important tribological phenomenon that has been studied intensively is the humidity dependence of friction. In the case of a-C:H, this is technologically important because a-C:H can typically achieve friction coefficients well below 0.1 and extremely low wear in inert environments, but friction coefficients and wear rates rise in the presence of humidity levels typically seen in ambient environments.\textsuperscript{32,44} A similar rise in friction with \textgreek{O}_2 pressure has also been reported, although higher \textgreek{O}_2 pressures are required, as shown in Figure 1.4.\textsuperscript{46} A better understanding of why this occurs could perhaps lead to strategies to prevent it. One study that is relevant to understanding the effect of environmental gases on friction involved reciprocating sliding on DLC in dry air ($\leq 1\%$RH) where a variable delay time was imposed between sliding passes. In that case, the friction coefficient rose with increasing delay time and the results were well-fit by a model where the friction coefficient was assumed proportional to a surface coverage of adsorbed gas molecules delivered at a rate described by Langmuir’s fractional surface absorption model.\textsuperscript{105–107} Other studies have also attributed the environmental dependence to physisorbed gas molecules.\textsuperscript{38,46,108} While this testing did not
examine the effect of humidity directly, it does demonstrate that adsorbed gases can increase frictional forces in DLC. Interestingly, there is a seeming contradiction between these results and the surface passivation theory of lubrication. Higher speeds with less gas exposure time between passes should favor the presence of dangling bonds that can form adhesive junctions with the counterface, thereby increasing friction. The resolution of the contradiction may be related to the fact that these tests were run with the superlubric form of hydrogen-rich a-C:H which can sustain low friction even in UHV, where typical a-C:H cannot.\textsuperscript{6,54}

![Figure 1.4: Effect of gas partial pressure leaked from UHV on the friction coefficient of self-mated a-C:H against a 4 mm ball at 21 mm/s. Adapted from Ref. 46.](image)

Unfortunately, present experimental methods cannot directly identify the mechanism by which humidity and other environmental gasses perturb the friction coefficient. For this, simulations are the best tool presently available.

**Applications of DLC’s**

The first major application of DLC’s was in the hard drive industry. It was recognized in the 1980s that thin layers of DLC provided substantially better wear protection for the magnetic
media of the disk than all materials used prior. This spurred a great deal of research interest on DLC’s to better understand how to further minimize wear and friction and provide even better protective overcoats to meet the ever increasing requirements imposed by increases in magnetic storage density. ta-C films are now used to protect the hard disk read/write head from wear as well. Starting in the late 1990s, deposition technologies became sufficiently inexpensive and reliable to produce coatings for more industries. The applications in commercial products included coatings for razor blades and diesel engine injectors. After initial use in the 1990’s in racecar engines where cost was less critical and lower friction of DLC-coated engine components also led to increased power, in recent years, DLC has been adopted as a protective coating for mass market automotive components including piston pins, piston rings, tappets, piston skirts, finger followers, and valve shafts. A selection of the DLC-coated components is shown in Figure 1. The excellent biocompatibility of DLC has led to DLC-coated medical products including arterial stents, urinary catheters, osteotomy screws, and surgical tools. One rather obvious application of diamond-like properties of DLC is in protective coatings for machining tools, and such products are available, especially for the machining of Al alloys. The diffusion barrier properties of DLC have led to commercialization of a rapid DLC coating technology for plastic beverage bottles that allows for a shelf life similar to glass bottles or aluminum cans. There are additional applications for which DLC’s show promise but have not yet been deployed commercially. These include strain gauges, where the precision is extremely high but there remains an unacceptable sensitivity to temperature, water faucet valve seals, molds for glass lenses, and coatings for spacecraft components exposed to reactive atomic oxygen in low earth orbit.
Figure 1.5: Selection of automotive engine components now commercially available with DLC coatings. Adapted from Ref. 67.

**Development of silicon-oxide doped hydrogenated amorphous carbon (a-C:H:Si:O)**

Early work indicated several attractive characteristics of films doped with SiOₓ, henceforth referred to as silicon oxide-doped hydrogenated carbon (a-C:H:Si:O): lower residual stress than equivalent a-C:H’s (in terms of sp³ and C/H ratio),¹²³,¹²⁴ improved thermal stability,¹⁵,⁸²,⁸⁴ and a purportedly reduced dependence of friction on the humidity of the sliding environment.⁵⁰,⁸¹,¹²⁵ All three of these characteristics have substantial technological applicability, and indeed a-C:H:Si:O is commercially available with a widening range of commercial applications including automotive engine protective coatings, gear coatings, coatings for metal forming tools, and molds for plastic part formation.⁸⁵
a-C:H:Si:O may be deposited via a variety of deposition techniques. The most widely cited forms are deposited with plasma enhanced chemical vapor deposition (PECVD) using hexamethyldisiloxane (HMDSO) as the precursor gas, which contains all of the elemental constituents. In this deposition technique, the HMDSO is ionized by a hot filament, or a radio frequency or microwave source, and the resulting ions are accelerated by a 50-200 V DC negative bias on the substrate. The resulting composition and structure of the film may be controlled via changes to the deposition conditions (substrate bias, gas pressures, etc.). An example of this type is discussed extensively in Chapter 2. A related deposition technique referred to as plasma immersion and ion implantation deposition (PIIID) may also be used to synthesize these films. In this case, the substrate is not continuously DC biased, but rather subjected to a pulsed DC bias in the kV range with a kHz duty cycle. Such films may be produced with similar properties to those produced via PECVD, but can also be deposited conformally on high aspect ratio substrates because the delay between pulses allows for ions to diffuse around the substrate such that ions always arrive normal to the local substrate orientation. An a-C:H:Si:O produced via PIIID will be the primary focus of this thesis. Figure 1.6 presents a schematic representation of the PIIID deposition process.

Some work has been undertaken to understand the attractive properties that arise with SiO₅ doping. The thermal stability of a-C:H:Si:O has been interrogated in several studies. Such work has demonstrated that it is not the pure thermal stability which is improved by a large margin, but rather the thermo-oxidative stability. When DLC is heated in the presence of
O₂ or H₂O, the carbon can react with environmental species to form gaseous CO₂ and CO,
causing the film thickness to erode at substantial rates.¹²⁹⁻¹³¹ SiOₓ doping leads to the formation
of a thin SiO₂ surface layer which acts as an oxygen diffusion barrier, protecting the underlying
a-C:H:Si:O from further oxidative attack.⁸²,¹³²

The mechanisms for the reduced residual stress is less well-understood. It has been
hypothesized that the source of this reduced stress relates to the microstructure of the film. At
one time, the a-C:H:Si:O was referred to as diamond-like nanocomposite (DLN) due to evidence
that preferred bonding of the Si to O and C to H led to a structure composed of fully
independent and interpenetrating sublattices of SiOₓ and a-C:H. Subsequent spectroscopic
studies have revealed that these sublattices are not fully independent, with some bonding
between C and Si/O and bonding between Si and H. Nevertheless, such bonds are a minority in
a-C:H:Si:O, and the model of independent sublattices remains a reasonable approximation. It
was hypothesized the longer equilibrium bond lengths of the SiOₓ lattice exert a tensile stress
within the lattice counteracting the compressive stress of the a-C:H sublattice, resulting in a
reduction of the overall compressive stress. There is one molecular dynamics study which
supports this hypothesis by showing that the incorporation of Si into DLC reduces the fraction of
strained C-C bonds present in the film.⁸⁴ Finally, a reduced dependence of friction on
environmental humidity relative to a-C:H has been achieved in some cases.⁸⁸ Some simulation
work suggests the presence of Si at the DLC surface can increase the propensity for H₂O surface
adsorption thereby improving the tribological response under varied environments.⁹⁵,⁹⁶ It
should also be noted that not all modifications to a-C:H via SiOₓ doping are technologically
advantageous. Increasing the amount of SiOₓ in the structure of a-C:H:Si:O leads to some
reduction in the modulus and hardness and an associated increase in the wear rate of a-
C:H:Si:O.¹²⁵

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INTRODUCTION

As discussed in Chapter 1, amorphous carbon (a-C) films have been successfully used in a wide range of technological applications, including as protective coatings for hard disks, machining tools, razor blades, and automotive engine components. In particular, the possibility of depositing a-C on a variety of substrates and obtaining continuous, pinhole-free films with ultralow roughness and thickness played a crucial role for the use of a-C as an overcoat material in hard disks. In spite of these successes, several critical challenges limit the wider use of a-C. In particular, in the case of hydrogenated amorphous carbon (a-C:H), the limited thermo-oxidative stability has raised concerns about the suitability of these materials for a variety of applications. For example, next-generation high-capacity hard disk drives will be based on heat-assisted magnetic recording (HAMR) technology, which incorporates a laser to locally heat a high-anisotropy magnetic medium to elevated temperatures (450-550°C) during the recording process. At temperatures relevant for HAMR technology, a-C:H rapidly degrades. In fact, degradation in oxygen-containing environments occurs at temperatures as low as 150°C. The goal in this initial phase of the thesis was to enhance the thermo-oxidative stability of a-C:H coatings by doping them with silicon and oxygen, while maintaining the possibility of depositing ultrathin films with ultrasmooth morphology. Silicon- and oxygen-containing amorphous hydrogenated carbon (a-C:H:Si:O) films were synthesized by plasma immersion ion implantation and deposition (PIIID) by a commercial collaborator, NCD Technologies. The deposited ultrathin, ultrasmooth films exhibited improved thermo-oxidative stability over a-C:H coatings, and even a-C:H:Si:O films deposited by plasma-enhanced chemical vapor deposition that were previously studied by our group.

Providing context for this work is that at elevated temperatures, a-C:H has been shown to degrade via a series of distinct pathways. It was shown that during vacuum annealing above 150°C, sp² sites in a-C:H rapidly diffuse and coalesce into larger, ordered sp²-rich regions. At higher temperatures, further degradation of a-C:H films occurs through the scission of sp³ C-H bonds and the breakage of sp³ C-C bonds. Both processes result in a progressive increase in the
fraction of sp²-bonded carbon in the films. Exposure to an aerobic atmosphere at elevated temperature leads to a different degradation pathway, where the material is rapidly eroded through the volatilization of carbon (through the formation of CO and CO₂).⁵,⁶

Hydrogenated amorphous carbon doped with silicon and oxygen (a-C:H:Si:O) has been shown to exhibit higher thermal and oxidative stability¹⁰,¹¹ including in work by the author.¹²,¹³ Our early work on a-C:H:Si:O demonstrated that a-C:H:Si:O films grown by plasma enhanced chemical vapor deposition with silicon and oxygen levels of, respectively, 6±1 at.% and 3±1 at.% exhibit a slightly enhanced thermal stability under high vacuum conditions compared to a-C:H (with similar fraction of sp²-bonded carbon and hydrogen content). Molecular dynamics simulations suggested that this slight enhancement in thermal stability is induced by the reduction of the number of strained carbon-carbon sp³ bonds in a-C:H:Si:O compared to a-C:H, which are more likely to break at elevated temperatures.¹²,¹³ The introduction of silicon and oxygen in a-C:H:Si:O was, however, found to drastically increase the thermo-oxidative resistance through the formation of a thin silica surface layer, which prevents the underlying carbonaceous phase to be eroded. a-C:H:Si:O films also exhibit low wear and friction over a wider range of environmental conditions compared to undoped a-C:H.⁹,¹⁴ It has also been shown to have high resistance to wear under high stress nanoscale sliding.⁸ These attributes make a-C:H:Si:O materials interesting for applications where extreme conditions are found, such as next-generation hard disks based on HAMR technology, automotive and spacecraft components, and MEMS devices.¹⁵–¹⁷

The most studied forms of a-C:H:Si:O material to date are deposited by plasma-enhanced chemical vapor deposition (PECVD) using siloxanes as precursor gases with or without additional reactive gases (e.g., CH₄, H₂, O₂) and possibly carrier gases (e.g., Ar).¹⁸–²¹ However, a-C:H:Si:O films can also be grown using multiple other plasma-based techniques.²²–²⁵ The use of other deposition techniques can overcome the major disadvantage of PECVD, namely the difficulty of depositing conformal films on components with complex shapes.²⁶ This is due to the fact that PECVD, as with most deposition technologies utilized for DLC synthesis,²⁷ involves a direct path from the source of the ions/plasma to the substrate, leading to nonuniformity of thickness and properties for three dimensional substrates.²⁸,²⁹ In contrast, plasma immersion
ion implantation and deposition (PIIID), by virtue of the temporal separation in pulses, allows ions to diffuse around the workpiece between the pulses (“ion immersion”), which then locally accelerate and implant the ions toward every surface. As a result, regardless of local substrate orientation, ions can impinge normal to the surface. Thus, in addition to the general advantages of substrate flexibility and no substantial heating of the substrate, PIIID provides the technologically-important ability to conformally coat surfaces with complex geometry.27,30,31

In the present work, the PIIID a-C:H:Si:O films were grown by a commercial collaborator. Films were deposited on silicon substrates and silicon AFM cantilevers with integrated tips. To provide context to the results concerning the thermo-oxidative stability of the PIIID a-C:H:Si:O films, the prior equivalent characterization of a commercial PECVD a-C:H:Si:O is presented.12–14

Experimental Methods
PIIID Film Deposition

The PIIID films discussed were deposited by NCD Technologies (Madison, WI, USA) on polished silicon single crystal substrates for 30 min, and on silicon AFM probes for 108 sec. Hexamethyldisiloxane (HMDSO, Sigma Aldrich, NMR Grade, ≥99.5%) was used as a precursor gas at 5 Torr. Plasma was generated via glow discharge from a thermionic emitter. The deposition itself was controlled by pulsing the substrate to -2.4 kV for 10 µs at a rate of 2 kHz. The substrate was not intentionally heated, but impinging ions are expected to raise its temperature to <200°C.

a-C:H:Si:O grown by radio frequency PECVD was analyzed for comparison purposes. 2 µm-thick PECVD-grown a-C:H:Si:O coatings were obtained from Sulzer Metco Inc. (Dylyn 180). These films were deposited using a proprietary procedure, whose details are described elsewhere.33–36 An annealing temperature of 450°C was chosen for this study because this is in the range of operating conditions for applications where a-C:H is excluded due to thermal degradation, but a robust variant of the material would be technologically attractive.
Annealing Experiments

To investigate the structural evolution of PIIID a-C:H:Si:O vs. temperature under high vacuum conditions (pressure <1 x 10^{-6} Pa), heating experiments were performed inside the X-ray photoelectron spectrometer (XPS) chamber or the near edge X-ray absorption fine structure (NEXAFS) spectroscopy endstation at the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory (Upton, NY, USA). All experiments were carried out using a-C:H:Si:O films deposited on silicon wafers.

For the annealing experiments performed inside the XPS chamber, the samples (6 x 6 mm²) were mounted in a holder (RHK Technology, Inc., Troy, MI, USA) that included a tungsten filament for radiative heating and a K-type thermocouple in contact with the sample for recording specimen temperature. The standard deviation of the annealing temperature was always below 0.5°C. The films were annealed at 450°C for 1 h and cooled after the anneal (heating and cooling rate: 10°C/min). The XPS spectra, whose acquisition required approximately 9 h, were collected after cooling the sample to below 40°C.

For the experiments carried out in the NEXAFS endstation chamber, the samples (~8 x 8 mm²) were mounted on a custom-made holder that included a tungsten filament for heating and a K-type thermocouple in contact with the sample for recording specimen temperature. The standard deviation of the annealing temperature was always below 2°C. The films were annealed at 450°C for 1 h. Since the acquisition of NEXAFS data only required 5 min, the spectra were collected without cooling the sample to room temperature (i.e., they were acquired at elevated temperature).

To investigate the surface structural evolution and chemical changes of a-C:H:Si:O vs. temperature under aerobic conditions, heating experiments were performed using hot plates. All tests were performed using a-C:H:Si:O films deposited on silicon wafers. The samples (~1 x 1 cm²) were annealed at 450°C. To monitor specimen temperature, a K-type thermocouple was put in contact with the sample surface. The standard deviation of the annealing temperature was 3°C. The relative humidity (27±3%) was continuously monitored during the annealing experiments (Humidity Meter 11-661-21, Fisher Scientific, Waltham, MA, USA). After being
annealed, the specimens were cooled down for 30 min and then characterized by multiple analytical techniques.

Film Characterization

Films were analyzed by optical microscopy, AFM, TEM (in the case of PIID a-C:H:Si:O-coated AFM probes), RBS/FRES, and XPS and NEXAFS spectroscopies. AFM measurements were performed in contact mode near zero load in an Asylum MFP-3D AFM using silicon AFM probes. TEM observations were performed with a JEOL 2100 HRTEM. XPS measurements were conducted in a customized laboratory-based environmental XPS chamber utilizing a VG Scienta R3000 electron energy analyzer. NEXAFS measurements were performed at Brookhaven National Laboratory’s National Synchrotron Light Source, beamline U7A. The C1s spectra in were first pre-edge normalized so that changes in carbon concentration are reflected in the peak intensity. Post edge normalization was applied as well, which removes the effect of differing carbon concentrations so spectral shifts can be compared. Additional details about the XPS and NEXAFS measurements and analysis are contained in the Supporting Information.

X-Ray Photoelectron Spectroscopy (XPS)

The chemistry of the near-surface region of silicon oxide-doped hydrogenated amorphous carbon (a-C:H:Si:O) was investigated by X-ray photoelectron spectroscopy (XPS) using a customized XPS spectrometer, extensively described elsewhere. The XPS spectrometer is equipped with a monochromatic Al Kα X-ray source with a beam diameter of 1 x 3 mm². The photoelectrons emitted from the specimen are collected with an electrostatic lens, whose axis is normal to the sample surface. After passing the hemispherical analyzer, the photoelectrons are detected by a two-dimensional MCP/CCD detector.

In the present work, the X-ray source was run at 30 mA and 12 kV, whereas the analyzer was operated in constant-analyzer-energy (CAE) mode. Survey spectra were acquired with the pass energy and step size equal to 200 eV and 1 eV, respectively. For the high-resolution (HR) spectra, the pass energy and step size were, respectively, 100 and 0.05 eV (full width at half
maximum (FWHM) of the peak height for the Ag 3d\textsubscript{5/2} equal to 0.57 eV). The curved slit at the entrance of the hemispherical analyzer has a width of 0.8 mm. The residual pressure in the analysis chamber was always below 1 x 10\textsuperscript{-6} Pa. The spectrometer was calibrated according to ISO 15472:2001 with an accuracy better than ±0.05 eV. The high-resolution spectra were processed using CasaXPS software (v2.3.16, Casa Software Ltd., Wilmslow, Cheshire, U.K.). An iterated Shirley-Sherwood background subtraction was applied before peak fitting using a linear least-square algorithm.\textsuperscript{38} No sample charging was ever observed for the PECVD films, as determined by checking the position of the carbon (C 1s) signal and of the valence band (this is expected since the samples have moderate electrical conductivity). Charging was observed for the PIIID films, both before and after annealing, which can occur in highly sp\textsuperscript{3} films such as tetrahedral amorphous carbon. Compensation for charging was accomplished by shifting the spectral binding energy scales equally for all high resolution spectra until the synthetic components common to multiple high resolution spectra (\textit{i.e.} C-O and C=O for C1s and O1s) attained the same intensity ratio.

The quantitative evaluation of XPS data,\textsuperscript{39,40} was based on the integrated intensity (\textit{i.e.}, the peak area in Cps x eV obtained from the original spectra after background subtraction and curve synthesis) using a first principles model and applying Powell’s equations.\textsuperscript{41} The inelastic mean free path (the mean distance traveled by electrons with a given kinetic energy (KE) between inelastic collisions in the material\textsuperscript{42}) was calculated using the TPP-2M formula.\textsuperscript{43}

All the XPS results reported here are mean values calculated from at least three independent measurements, with the corresponding standard deviation reported.

\textit{Near Edge X-Ray Absorption Fine Structure (NEXAFS) Spectroscopy}

Near edge X-ray absorption fine structure (NEXAFS) spectroscopic measurements were performed at the NIST/Dow endstation of beamline U7A at the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory (Upton, NY, USA). The photon source of this beamline is a bending magnet, and covers an energy range from 180 to 1100 eV for U7A. The photon flux is 2x10\textsuperscript{31} photons/second/0.1% bandwidth, and the resolution (∆E/E) is ~1 x 10\textsuperscript{-3}. All measurements were carried out in partial electron yield (PEY) mode and at a photon incidence
angle of 55° with respect to the sample source (the so-called “magic angle”) to suppress the effects related to the X-ray polarization. For the experiments described here, the entrance grid bias (EGB) of the channeltron detector was set to -225 V to enhance surface sensitivity and minimize the detection of Auger electrons that suffered from energy loss while travelling through the sample before being emitted into the continuum. The monochromator energy was calibrated using the carbon 1s-\(\pi^*\) transition of freshly-cleaved highly ordered pyrolytic graphite (HOPG, grade 2, SPI Supplies, West Chester, PA, USA), located at 285.5 eV. The spectra acquired at U7A were first normalized to the absorption current measured simultaneously from a gold mesh placed in the beamline upstream from the analysis chamber. After this pre-edge normalization, the spectra were normalized based on the absorption intensity in the post-edge (continuum) region (at 320 eV). In this way, variations in spectral intensity only arise from chemical changes and are independent of the number density of absorbing atoms.

The quantitative evaluation of the fraction of sp\(^2\)-bonded carbon in the specimens on the basis of NEXAFS data was performed. The methodology is based on the relative integrated intensity ratios of the C1s→\(\pi^*\) and C1s→\(\sigma^*\) peaks for the sample under investigation and for a reference specimen:

\[
f_{sp^2} = \frac{I_{sam} \pi^*(E)}{I_{sam} \sigma^*(E)} \frac{I_{ref} \sigma^*(E)}{I_{ref} \pi^*(E)}
\]  

Eq. 1

where \(I_{sam} \pi^*(E)\) and \(I_{ref} \pi^*(E)\) are, respectively, the areas of the C1s→\(\pi^*\) peaks for the sample and the reference, whereas \(I_{sam} \sigma^*(E)\) and \(I_{ref} \sigma^*(E)\) are the areas under the NEXAFS spectrum between 288.6 eV and 320 eV for the sample and the reference, respectively. As a reference, the spectrum of freshly-cleaved HOPG (100% sp\(^2\)-bonded carbon) sample was acquired with the X-ray beam incident at an angle of 40° to the sample surface to account for the \(\cos^2(\Theta)\) (\(\Theta\) angle between the X-ray beam and the sample surface) angular dependence of the \(\pi^*\) and \(\sigma^*\) resonance intensity as well as for the polarization factor of the impinging X-rays.\(^{44,50}\)
All the NEXAFS results reported here are mean values calculated from at least three independent measurements, with the corresponding standard deviation reported as the uncertainty.

*Rutherford backscattering and forward recoil elastic scattering analysis*

Rutherford backscattering spectroscopy (RBS) and forward recoil elastic scattering (FRES) analyses were performed on the plasma immersion and ion implantation deposited a-C:H:Si:O.

RBS measurements were made using 2.023 MeV He\(^+\) ions at normal incidence to the sample surface with the detector placed at a 170° scattering angle. The detector energy scale was calibrated using spectra acquired from a Pb-doped Al\(_2\)O\(_3\) sample. The experiment was modeled using SIMNRA software (v6.06, Max Planck Institut fur Plasmaphysik, Garching, Germany). Reported composition/thickness error is based on an analysis of the sensitivity of modeled spectra to composition/thickness changes in SIMNRA. A film thickness of 182±21 nm was calculated using an assumed density of 2.0 g/cm\(^3\).

FRES measurements were performed in a glancing geometry with 3.023 MeV He\(^{++}\) ions incident at 15° from the sample surface plane, and the detector placed at a scattering angle of 30°. A nominally 10 µm thick mylar stopper foil was used to attenuate scattered helium nuclei. The detector energy scale was calibrated by measuring the spectra of a gold sample with various incident ion energies and no stopper foil.\(^{51}\) A Kapton reference sample was used for calibration of the stopper foil geometry by measuring spectra with the stopper foil in place and varying the modeled mylar thickness in SIMNRA to achieve an accurate Kapton composition. DLCs are known to lose hydrogen during FRES measurements.\(^{52}\) To account for this effect, FRES spectra were acquired prior to RBS spectra, and FRES spectra from the a-C:H:Si:O at several ion doses were obtained sequentially. The measured hydrogen fraction was used to extrapolate back to the hydrogen present at zero dose, though hydrogen loss during the measurement turned out to be negligible.
Results

Optical microscopy (not shown) demonstrates that the films are homogenous with no signs of delamination.

Figure 2.1. (a) AFM contact-mode topographic images of PIIIID-grown a-C:H:Si:O films before and after annealing at 450°C under aerobic conditions (31±3% RH in air) or in high vacuum (HV) for 1 hour; (b) TEM images of an atomic force microscope (AFM) probe coated with a-C:H:Si:O (PIIID-grown; thickness: 15 nm).

Figure 2.1a shows the sample morphology as captured by atomic force microscopy (AFM) for the as-grown sample as well as after annealing at 450°C for 1 hr under high vacuum and aerobic conditions. The root mean square roughness of the as-grown sample is exceptionally low, 0.16±0.01 nm across a 1x1 µm² area, even for ultrathin films (5 nm thick, as confirmed by X-ray reflectivity measurements). The roughness does not significantly change upon annealing, either in high vacuum or aerobic conditions. Transmission electron microscopy (TEM) characterization of silicon AFM probes coated with a-C:H:Si:O deposited by PIIIID (Figure
2.1b) provides evidence that a-C:H:Si:O films can be deposited in a conformal manner on high aspect ratio, high curvature structures. In addition, the TEM analysis indicates that PIIID-grown a-C:H:Si:O films are a fully amorphous solid solution without any inclusions or phase separation. This result agrees with friction force microscopy (FFM) images (not shown) acquired simultaneously with the topographic maps displayed in Figure 2.1a: the absence of any contrast in FFM maps was observed for both as-received and annealed samples, thus indicating surface chemical and structural homogeneity.

Rutherford backscattering spectroscopy (RBS) and forward recoil elastic scattering (FRES) analyses were performed, yielding a bulk film composition of \([C] = 30\pm{10}\text{ at.\%}, [Si] = 23\pm{5}\text{ at.\%}, [O] = 11\pm{4}\text{ at.\%}, \text{and } [H] = 36\pm{4}\text{ at.\%}.\)

![Figure 2.2.](image)

**Figure 2.2.** (a-b) High-resolution Si 2p XPS spectra of PECVD- and PIIID-grown a-C:H:Si:O acquired before and after annealing at 450°C under aerobic conditions (RH=31±3%) or in high vacuum (HV). Colored lines are curve fits; (c) apparent composition (calculated from XPS data, i.e., without accounting for hydrogen) of PIIID- and PECVD-grown a-C:H:Si:O before and after annealing at 450°C under aerobic conditions (RH=31±3%) or in high vacuum.
To study the evolution of the films’ chemistry and structure under thermal and thermo-oxidative stress, the films were analyzed with X-ray photoelectron spectroscopy (XPS) before and after annealing. In the as-grown material, Si is present in different oxidation states, from +1 to +4, as seen in Figure 2.2a, but with Si(I) (and/or SiC bonding which occurs at the same bonding energy) dominating. Under vacuum annealing, the silicon bonding configuration remains relatively unchanged, with only a slight increase of silicon atoms in higher oxidation states. This is consistent with the compositional quantification, which shows no significant changes in composition. Under aerobic annealing, substantial variations in the composition of the near-surface region were detected: the carbon concentration largely decreased, while the oxygen concentration increased drastically (Figure 2.2b). The Si 2p XPS analysis also indicated a large increase in the fraction of silicon atoms in higher oxidation states upon annealing under aerobic conditions.

The comparison of the outcomes of the XPS characterization of PIIIID-grown and PECVD-grown a-C:H:Si:O films before and after identical annealing conditions under high vacuum and under aerobic conditions revealed significant differences. First, the PIIIID-grown film initially contains a larger concentration of silicon and oxygen. Second, upon high vacuum annealing, PECVD-grown films showed an increase in the apparent concentration of oxygen with a significant increase in the fraction of silicon atoms in high oxidation states (+3 and +4, see Fig S.1). These changes were much less pronounced in PIIIID-grown films annealed under high vacuum. Third, upon annealing PECVD-grown films in air, a drastic depletion of carbon (from 80 to <10%) in the near-surface region was observed with the formation of a stoichiometric silicon dioxide layer (note: 97±1% of the silicon atoms in the near-surface region of air-annealed PECVD-grown films was in oxidation state +4). On the contrary, with PIIIID-grown films, a significant fraction of Si atoms remained in lower oxidation states (only 48±1% of the silicon atoms in the near-surface region of air-annealed PIIIID-grown films was in oxidation state +4) and a large fraction of carbon remains in the near-surface region. Thus, the XPS results demonstrate that the surface chemistry of the PIIIID-grown film changes to a much lesser extent than that of PECVD-grown a-C:H:Si:O upon annealing under both high-vacuum or aerobic conditions. Importantly, the thermo-oxidative stability of a-C:H:Si:O films (both PECVD- and PIIIID-grown) is
much higher than that of undoped a-C:H, which quickly erodes under similar aerobic annealing conditions.\textsuperscript{5,6}

To gain a thorough understanding of the carbon hybridization states and bonding configurations in the surface region of the films, synchrotron-based near edge X-ray absorption fine structure (NEXAFS) spectroscopic measurements were performed. In general, C1s spectra of C-based solids are characterized by a well-defined peak near 285 eV due to the C1s→\pi* transition for disordered carbon\textsuperscript{44,53} whose intensity is directly proportional to the sp\textsuperscript{2} content of the analyzed region.\textsuperscript{45,49,54} A broader extended structure appears between 286 and 330 eV, which is due to the C1s→\sigma* transition for sp\textsuperscript{2} and sp\textsuperscript{3} bonding.\textsuperscript{44,53} Due to the large distribution of bond angles and lengths in the amorphous structure, this spectral feature is broad and relatively featureless. The presence of C=O, and C-H bonds in the sample near-surface region could both contribute to the spectral intensity observed between 286.7 and 288.5 eV. An absorption peak was detected at 289 eV, which can be attributed to C-Si,\textsuperscript{55} C-O, and/or COOH bonding.\textsuperscript{44,56}
Most importantly, NEXAFS spectroscopy allowed the quantification of carbon atoms in the sp³ hybridization state and the variation of this quantity upon annealing under high vacuum and aerobic conditions. For the as-grown film, the sp³ fraction is calculated to be 78±3%, indicating that PIIIID-grown a-C:H:Si:O films have a significant diamond-like character.
Upon vacuum annealing, a modest decrease in sp\(^3\) fraction (from 78±3% to 61±3%) was detected. This can be due to the thermally-induced scission of C-H, C-Si, and C-C bonds.\(^{13,57}\) Changes during air annealing are more pronounced: a significant decrease in the intensity of the post-edge region (Figure 2.3a) was observed, which indicated a decrease in the number density of absorbing carbon atoms, in agreement with XPS results. In spite of the variation in surface chemistry upon annealing in air, the fraction of carbon atoms in the sp\(^3\)-hybridization state does not significantly change. This might be due to the energetically-favorable reaction of oxygen with sp\(^2\)-bonded carbon, which is then selectively volatilized.\(^{58,59}\)

Similar NEXAFS measurements were performed on the PECVD-grown a-C:H:Si:O films. While the NEXAFS C1s→\(\pi^*\) spectral features were similar to those found in the PIIIID-deposited films, the initial sp\(^3\) fraction was notably lower for PECVD films (58±3%). This finding indicates that the higher fraction of silicon atoms, the greater the stabilization of carbon atoms in the sp\(^3\) hybridization state. This influences the resulting thermo-oxidative stability of the material: while for PIIIID films the sp\(^3\) fraction only changed from 78±3% to 61±3%, for PECVD a-C:H:Si:O films the sp\(^3\) fraction drops substantially to 36±3% upon vacuum annealing. It should be noted that the PECVD a-C:H:Si:O already possesses a greater degree of pure thermal stability under vacuum annealing than an undoped a-C:H by the metric of activation energy for sp\(^3\)→sp\(^2\) C rehybridization.\(^{13}\) The measured changes in carbon hybridization ratios are summarized in Figure 2.4.
Air annealing of the PECVD film led to a large drop in C1s intensity, in agreement with XPS results as well as a dramatic enrichment in sp³ content, to 91±3%. The enrichment in sp³ is a result of the selective oxidation of the sp² C fraction within the film. The fact that such an enrichment did not occur in the PIIID films is a result of the fact that carbon in the PIIID film was more stable against oxidative stress in general.

Conclusions

In summary, we demonstrated that a-C:H:Si:O films with a high Si content (37±1 at.%) can be grown by PIIID. These homogenous, ultrasmooth films can be deposited conformally at very small thicknesses (down to 5 nm thick films) on high aspect ratio substrates (AFM probes). The characterization of the surface chemistry and structure revealed that PIIID-grown a-C:H:Si:O films have a higher silicon concentration and fraction of sp³-bonded carbon than commercially-available PECVD-grown films. The analytical investigation of the chemical changes and structural transformations occurring in the near-surface region of a-C:H:Si:O films upon annealing under high vacuum conditions or aerobic conditions revealed a higher thermo-oxidative stability for PIIID-grown films compared to PECVD-grown coatings, and much higher than a-C:H coatings which evaporate at a rapid rate under the annealing conditions here.\textsuperscript{5,6}
The high thermo-oxidative stability demonstrated for PIIID a-C:H:Si:O in this study can make this material attractive for a variety of applications where the current selection of a-C:H variants are insufficiently robust, such as next generation hard disk drives (HDDs), solar power, automotive, and spacecraft component coatings. The remainder of this thesis will focus on the characterization of the tribological response of this PIIID-grown a-C:H:Si:O.

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CHAPTER 3 - Macroscale Tribological Response and Tribofilm Characterization

Introduction

The source of the low friction behavior of DLCs against a variety of counterfaces has been investigated previously. As discussed in Chapter 1, two primary mechanisms are well-accepted as important to friction reduction. The first is surface passivation of dangling carbon bonds with species such as hydrogen or hydroxyl groups.\textsuperscript{1,2} This passivation changes the interaction with the counterface from one with numerous covalent bonds across the interface, similar to the bonding within the bulk of the DLC that produces attractive mechanical properties, to one with primarily van der Waals interactions which lowers friction substantially.\textsuperscript{1,3–9} In the case of hydrogenated DLCs, the passivating species can be hydrogen from the film itself, allowing for low friction in inert environments. For non-hydrogenated DLC’s low friction only occurs in a reactive environment (e.g. humid air) which can react with the DLC to passivate dangling surface bonds.\textsuperscript{1,10}

The second important mechanism is the formation of a transfer film on the counterface composed of worn material transferred from the DLC. Such films are referred to as tribofilms throughout this thesis, since interfacial chemistry controls their growth and structure.\textsuperscript{6} Various analytical techniques have been applied to study tribofilms formed by DLC films.\textsuperscript{11–15} From these studies it has been inferred, often based on Raman spectroscopy, that tribofilms have a higher fraction of sp\textsuperscript{2}-bonded carbon than the original DLC. Some authors have suggested that substantial graphitization is present in tribofilms, activating the primary friction reduction mechanism in graphite: easy shear between the graphene sheets which make up the graphite.\textsuperscript{4,11,12} (Note that, confusingly, some authors use the term “graphitization” loosely, where they only mean to suggest that conversion from sp\textsuperscript{3}- to sp\textsuperscript{2}-bonded carbon is occurring, as opposed to ordering into crystalline graphite). However, such conclusions have not been reached for all DLC tribofilms, and one recent in-depth study using electron energy loss spectroscopy (EELS) found enrichment of C-H bonding in an a-C:H:Si:O tribofilm, leading the authors to suggest the tribofilm possessed a polymeric structure.\textsuperscript{16}
The limited thickness and lateral size of tribofilms together with the usual curvature of the substrate they are present on have inhibited a careful investigation of their mechanical properties, while significantly hampering exhaustive, multi-technique structural and chemical characterization. Most reported thicknesses of DLC tribofilms are below 100 nm. Metal-doped DLCs can lead to thicker tribofilms, but the tribofilms are composed predominantly of metal, thus hindering the possibility of generalizing any conclusion regarding their structure/chemistry/mechanical properties to other DLCs.

At present, while the presence of a tribofilm is empirically known to be important to achieving low friction in a variety of carbon-based solid lubricant systems, even including diamond, the mechanism by which they facilitate low friction is not well established. A primary difficulty in better understanding their relevance to the tribological response is a lack of detailed characterization to understand their structure and properties. To this end, this study provides detailed tribofilm characterization, especially of mechanical properties via nanoindentation to link the nanomechanical properties of tribofilms with their structure.

**Film Composition Measurements**

The silicon- and oxygen-containing hydrogenated amorphous carbon (a-C:H:Si:O) films characterized for this study were grown using plasma immersion and ion implantation deposition (PIIID) by NCD Technologies using hexamethyldisiloxane as a precursor gas. The composition of the near-surface region (<15 nm), excluding hydrogen, was estimated with X-ray photoelectron spectroscopy (XPS) to be 50.2±0.1 at.% C, 20.6±0.2 at.% Si, 29.1±0.2 at.% O.

Forward recoil elastic scattering (FRES) analysis was performed on the PIIID-grown a-C:H:Si:O. The PIIID-grown a-C:H:Si:O was too thin (40 nm) to accurately determine the bulk composition with RBS. FRES measurements were performed in a glancing geometry with 3.023 MeV He ion incident at 15° from the sample surface plane, and the detector placed at a scattering angle of 30°. A 10 µm thick mylar stopper foil was used to attenuate scattered helium nuclei. The detector energy scale was calibrated by measuring the spectra of a gold sample with various incident ion energies and no stopper foil. A Kapton reference sample was used for calibration of the stopper foil geometry by measuring spectra with the stopper foil in place and
varying the modelled mylar thickness in SIMNRA until an accurate Kapton composition was obtained. DLCs are known to lose hydrogen during FRES measurements. To account for this effect, FRES spectra from the a-C:H:Si:O at several ion doses were obtained sequentially. For the particular samples analyzed, hydrogen loss was negligible across the range of sampled doses (2-18 µC). Forward recoil elastic scattering (FRES) yielded a hydrogen fraction of 47±2% using the ratio of C/Si/O determined with XPS for modelling. Based on this, the atomic concentration of each element would be 27±2% C, 11±2% Si, 15±2% O, and 47±2% H.

The carbon sp³ fraction was measured to be 73±5% with near-edge X-ray absorption fine structure spectroscopy (NEXAFS). Further details about the XPS and NEXAFS analyses are contained in Chapter 2.

Experimental Methods for Mechanical Property and Tribometry Measurements and Post-Tribometry Analysis

The a-C:H:Si:O was subjected to ball-on-flat reciprocating tribometry using a 6 mm diameter, 52100 polished bearing steel ball at a normal load of 0.5 N and a sliding speed of 3 mm/s. The steel balls were cleaned by ultrasonication in acetone, then methanol. The sliding tests were performed at least five times in each of three environments: ambient air (measured relative humidity (RH) was always 40-60%), blowing N₂, and blowing dry air. The dry environments were achieved by arranging two gas nozzles in close proximity to the sliding interface while blowing 5 L/min of gas. Hygrometer readings between the gas nozzles showed that RH could be reduced to <6%.

AFM measurements of the PIIIID a-C:H:Si:O tribofilm morphology were performed in amplitude modulation (tapping) mode using a Bruker Icon AFM (Bruker Co., Billerica, MA). Images were flattened using line-by-line leveling as well as subtraction of a best-fit parabola after masking out the tribofilm to remove the curvature of the steel ball. SEM imaging and energy-dispersive X-ray (EDX) spectroscopic measurements were performed with a FEI Quanta
600 FEG Mark II Environmental Scanning Electron Microscope (ESEM). The EDX measurements shown were acquired sequentially with identical acquisition parameters and an accelerating voltage of 15 kV.

Raman measurements were performed on the as-received PIIID a-C:H:Si:O as well as tribofilms grown in the three different environments. These measurements were made using a near-field scanning Raman spectrometer (NT-MDT NTGRA\textsuperscript{TM} Spectra Upright, NT-MDT Co.) with a 532 nm laser, focused to a spot size of diameter 1 µm with a total laser power of 25.9 µW and 250 s acquisition time.

Nanoindentation measurements were performed using a TI 950 Triboindentor (Hysitron Inc., Minneapolis, MN). The indentation method was a continuous stiffness measurement using the Hysitron nanoDMA module and a diamond cube corner tip. The load sequence incorporated a single loading segment, at an exponential loading rate to achieve a constant strain rate and therefore avoid possible varying viscoplasticity effects across the depth range of each indent,\textsuperscript{21} to a maximum load of 500 µN. Superimposed on top of the loading sequence was a 220 Hz sinusoidal modulation controlled by feedback to a target amplitude of <5 nm. This modulation allowed for the continuous determination of the reduced modulus across the depth of the indent.\textsuperscript{22} The area function of the indenter tip was calibrated by indenting fused quartz, then fitting the area function coefficients to provide the best agreement with reference values of reduced modulus and hardness. The accuracy of the area function was checked by indenting a single crystal aluminum sample.

A focused ion beam (FIB) cross section of a tribofilm was milled for TEM imaging in the FEI Quanta 600 FEG Mark II ESEM using the standard milling and liftout procedure using deposited Pt pads to protect the specimen from Ga ion beam damage.\textsuperscript{23} The cross section was imaged in a JEOL 2010F TEM/STEM (JEOL USA Inc., Peabody, MA) using 200 kV electrons. The tribofilm, along with a Si AFM probe which had been coated with a-C:H:Si:O with nominally identical deposition parameters to the film coated on the flat, was subsequently imaged in a JEOL 2100F equipped with a Quantum GIF and K2 direct detection camera (Gatan, Pleasanton, CA) for EELS.\textsuperscript{24} Imaging and EELS were performed in scanning TEM (STEM) mode with an accelerating voltage of 200 kV, the probe was formed with a 40 µm condenser aperture. The probe current
was measured to be ~22 pA using the direct detection camera in counting mode as described in Ref. 24. Overall dose to any portion of the sample was kept below $2 \times 10^6 \text{ C/m}^2$ to prevent damage which would bias the spectroscopic results; the low-noise direct detection system allows for high quality spectra with less electron dose compared to charge-coupled detectors. This dose was below the threshold values where appreciable damage was observed in other studies of DLCs \textsuperscript{25} and even soft polymers.\textsuperscript{26} EELS compositional maps were produced from spectrum images taken across the indents. Displayed individual EELS spectra were produced by averaging dozens of spectra from particular regions of the EELS maps, after correcting for energy scale shifts using the position of the zero-loss peak and performing Fourier-ratio deconvolution as function of local sample thickness to reduce convolution of the low loss spectrum with the core edge spectra due to plural scattering.\textsuperscript{27}
Representative tribometry test results for the a-C:H:Si:O film are plotted for three different environments in Figure 3.1. Due to different wear rates in the different environments, the 40 nm thick film would wear out after different numbers of cycles. The tests shown in Figure 3.1 were all terminated shortly prior to the film wearing out. Run-in to steady state friction was

![Graph](image)

**Figure 3.1:** a) Representative ball on flat tribometry results for different sliding environments utilizing a hardened steel ball and PIID-grown a-C:H:Si:O film on Si(100) substrate. b) Width of a-C:H:Si:O wear track, as measured by calibrated optical microscope, as a function of the number of sliding cycles. Error bars show the spread of data where multiple wear tracks were measured.
fast, with steady state friction achieved in all environments within 20-30 cycles. The steady state friction coefficient in ambient air (45% RH) was substantially higher than for blowing dry air or \( \text{N}_2 \), with a value of 0.14±0.02. This implies that humidity is primarily responsible for an increased friction coefficient. These results are typical of hydrogenated DLCs, which have friction coefficients below 0.1 in inert environments, with higher values (up to 0.4) in humid environments.\(^{28}\)

The width of the wear tracks was measured via optical microscopy at various numbers of cycles for the three environments. Error bars indicate the spread of measured data where multiple tests were performed. The nominal Hertzian contact diameter, calculated for the ball diameter and steel and Si substrates, is displayed for reference. For the cases of humid air and dry air, the wear track width was similar to the nominal Hertzian radius regardless of the number of test cycles. For tests in blowing dry \( \text{N}_2 \), the wear track width grew well beyond the Hertzian radius, with an increasing trend with the number of cycles. There are several possible explanations for this behavior, including shearing of tribofilm out of the contact either due to low shear strength in the bulk of the tribofilm or poor adhesion to the steel counterface, or squeezing of tribofilm out of the contact due to its low hardness and/or viscoplastic deformation. Despite the increasing width of the wear track in the blowing \( \text{N}_2 \) case, the depth of the wear track grew slowest in this environment, as shown by the long film endurance of the a-C:H:Si:O film in blowing \( \text{N}_2 \) shown in Figure 3.1a.

As discussed in Chapter 2, one advantage of doping DLCs with Si and O is an improvement in thermal stability, as demonstrated through compositional and structural stability after annealing in vacuum or air.\(^{29-32}\) To confirm that this stability also preserves the tribological response in the PIIIID-grown a-C:H:Si:O, tribometry testing under the same conditions as the tests above was applied to films that were previously annealed at 350°C for 1 hr. in ambient air (42±1%RH). Under such conditions, a-C:H films would be largely if not totally destroyed. For a-C:H:Si:O, air annealing caused partial film delamination due to thermal expansion mismatch between the a-C:H:Si:O and the substrate. Although this clearly created a non-ideal film geometry, testing was nonetheless conducted to see how the film would behave tribologically. Results of sliding experiments in ambient air (36±1%RH) and blowing \( \text{N}_2 \) are presented in Figure 3.2a. In some
tests, the friction coefficient rose to large values, presumably due to the high-friction tribocouple between steel and Si that occurs in the delaminated regions which are clearly visible in Figure 3.2b. Surprisingly, in several of the cases, the steady state friction coefficient was similar to that achieved for the unannealed films in equivalent environments, indicating that (a) gaps in the film do not prevent good tribological behavior from occurring, and (b) the Si and O doping preserves the low friction behavior of the films even after severe thermooxidative stress.

Figure 3.2: a) Ball on flat tribometry results for a-C:H:Si:O film after 60 min, 350°C annealing in air. b) Optical microscope image of wear tracks made in laboratory air and surrounding a-C:H:Si:O film. Gray regions are exposed Si substrate. c) Optical microscope images of steel balls upon completion of the tribometer tests. These images show differences between transfer film for a case where the friction remained low throughout the test (Run 1) vs. a case where low friction was lost (Run 5). d) Triboscopy image of the evolution of the friction coefficient as a function of both cycle number and wear track position during Run 2.
To understand why the friction rose in some cases but not others, optical microscopy of the steel balls after testing provides an explanation. In the cases where friction was high at the end of testing, the counterface appeared to be stripped of its tribofilm, whereas substantial tribofilm remained in all cases where the friction coefficient remained low. Representative examples are presented in Figure 3.2c. Even in cases where the friction coefficient remained low, optical microscopy showed (Figure 3.2b) that all or nearly all of the a-C:H:Si:O had been removed from the Si flat. Surface-sensitive spectroscopy would be required to confidently assert that all material had been removed, and there was discoloration in the wear tracks from testing in N₂ which suggests adhesive transfer of some tribofilm back onto the Si in the wear tracks for that environment (Figure 3.3). To examine the dynamics occurring during testing, a triboscopy map of Run 2 is presented in Figure 3.2d which shows the friction coefficient as a function of position in the wear track and cycle number during the test. This representative result shows that at the start of testing there is substantial inhomogeneity of response across the wear track (Y-axis), with the friction decreasing and becoming more homogenous throughout the test (+X direction). This is interpreted as due to bare steel on exposed Si regions early in the test, but a decrease in overall friction and inhomogeneity as the tribofilm grows on the steel surface. These results reiterate the importance of transfer film to achieving low friction in this tribological system.
Figure 3.3: Wear tracks produced during blowing N$_2$ tribometer tests of 350°C 1hr. air annealed PIIID a-C:H:Si:O. Material has been transferred from the 52100 steel ball to the bare Si in the wear tracks.

Motivated by these tribometer tests where friction would remain low despite the failure of the a-C:H:Si:O and its complete removal from the wear track, a test of the lubricity of the tribofilm was performed. A $\frac{1}{4}$” diameter 52100 steel ball was slid on a-C:H:Si:O at 0.1 N normal load for 300 cycles in ambient conditions, then the steel ball (with newly-grown tribofilm) was moved to a bare Si(100) wafer where the same test was performed. The tests were performed sequentially, and the RH was 11±1% during all three tests. The results of this experiment, along with a control test sliding a new $\frac{1}{4}$” 52100 ball on the same Si(100) wafer are shown in Figure 3.4a. The friction coefficient in the tribofilm/steel on Si(100) test remains below 0.3 for >200 cycles before rising to a value similar to the bare steel on Si(100) test. The fact that low friction...
is maintained for hundreds of cycles confirms that the tribofilm effectively lubricates the Si/steel contact. It also indicates that velocity accommodation (i.e. specifically where in the materials adjacent to the sliding interface relative motion occurs) primarily occurs either within the tribofilm or at the tribofilm/substrate interface. Additionally, as shown in Figure 3.4b, for the tribofilm/steel on Si test, the friction coefficient was not homogenous across the wear track, but in fact was much lower near the center of the wear track than at the edges, with the friction becoming more homogenous as the test proceeded. We hypothesize that some fraction of the tribofilm is transferred to the center of Si track upon first contact with the ball at this location, leading to lower friction in the center of the track.

Figure 3.4: a) Results of three tribometer tests sliding ¼” diameter 52100 steel balls at 3 mm/s on 3 mm track with 0.1 N normal load. Schematics of contact geometry are included in legend for clarity. The steel + tribofilm test was performed with the same steel ball as the steel on a-C:H:Si:O test. The steel on Si test was performed with a new steel ball. b) Single cycle traces of lateral force/normal load for the steel + tribofilm test showing the evolution of friction force and its dependence on track position. For
reference, black lines show the lateral forces present for the steel on a-C:H:Si:O test after steady state was achieved.

Additional fluctuating environment tests were performed on the as-deposited films to see if friction could change reversibly with the sliding environment after growth of the tribofilm, as has been observed in previous studies of DLC tribology.\textsuperscript{34-36} The tests were performed by turning the blowing N\textsubscript{2} on and off. A representative test is shown in Figure 3.5. Indeed, the friction dependence on the environment is reversible for this a-C:H:Si:O.

![Friction vs. cycle number for tribometer test with intermittent blowing N\textsubscript{2}. Vertical dotted lines indicate when N2 blowing started or stopped. The horizontal dotted lines indicate the steady state friction measured during separate tests in ambient air (red) and blowing N2 (blue).](image)

Figure 3.5: Friction vs. cycle number for tribometer test with intermittent blowing N\textsubscript{2}. Vertical dotted lines indicate when N2 blowing started or stopped. The horizontal dotted lines indicate the steady state friction measured during separate tests in ambient air (red) and blowing N\textsubscript{2} (blue).
Tribofilm Characterization

Tribofilms obtained during controlled-atmosphere tribometer testing were initially characterized with tapping-mode atomic force microscopy. AFM images of tribofilms grown in blowing N₂ and ambient air are shown in Figure 3.6. The tribofilms are exceptionally thick, with maximum thicknesses ranging from 500 nm to 2 µm.

![AFM Images](image)

**Figure 3.6:** a) and b) AFM topographic images of tribofilms formed during 500 sliding cycles in blowing N₂ and 50 cycles in air, respectively. The yellow line in (a) shows the approximate position of the TEM cross section shown in Figure 3.17. c) and d) Profiles of the linescans shown in (a) and (b), respectively.

Though rarely reported, DLC tribofilm thicknesses in the literature are generally 100 nm or less. 13,37–39 Exceptions exist, but involve unique situations such as a metal-doped DLC where the tribofilm was primarily metal 17 and an undoped DLC sliding in a refrigerant gas environment. 40 The roughness of the films was 33±11 nm over 2.5x2.5 µm², as measured by sampling 3 regions from a film grown in each of the three sliding environments. Topographic characterization of the films was attempted with white light interferometry which showed oscillatory thicknesses across the film, which are consistent with interference artifacts observed.
in thick transparent films. Figure 3.7 shows a comparison between topographic measurements of the same tribofilm made with AFM and white light interferometry.

**Figure 3.7:** AM-AFM image (a) and linescan (b) of tribofilm produced after 100 sliding cycles in ambient air. White light interferometry image (c), linescan (d), and camera image (e) of the same tribofilm produced by the Zygo NewView 6300 interferometer.
Tribofilm Mechanical Properties

To examine the mechanical properties of the tribofilms, nanoindentation was performed. Quasistatic indents using a Berkovich tip and a load function with 43 load/unload segments exhibited, universally, a substantial degree of hysteresis in load vs. contact depth plots. This is illustrated in the graph inset in Figure 3.8a. Instead of tracing the same path during reloading after an unload segment, as would be expected for a purely elastic response, a loop was formed. Such behavior has been observed previously and has been attributed to phenomena such as reverse plasticity and reversible phase transitions.42–44 Another possibility is a viscous response, which can produce such hysteresis due to the dissipation inherent in viscous mechanical deformation.45,46

Additionally, indents could be difficult to locate in AFM imaging despite final indenter-measured contact depths typically in excess of 200 nm. To investigate further and ensure plasticity during the indenting process (a requirement for measured hardness values to have validity), indents were performed with a sharper cube corner tip. Amplitude modulation (tapping mode or AM-AFM) AFM imaging was performed on the indents immediately after indenting and again after some weeks. The results for a single indent (with estimated H = 3.2 GPa and E* = 24 GPa) are presented in Figure 3.8b,c. Over the course of 27 days, the indent recovers 18% of its depth. Eight additional indents in the same pattern were analyzed in this fashion. All but one showed measurable recovery, with an average depth recovery of 19 ± 12%. The AFM was calibrated in all three axes prior to these measurements with a calibration grating, and the height of a particular surface protrusion was measured at both times to confirm that the Z-calibration remained valid. Similar indent recovery has been observed frequently in the past for other materials and is generally attributed to viscoelasticity or viscoplasticity.47–54
Figure 3.8: a) Example of substantial unload-reload hysteresis frequently observed for quasistatic tribofilm indentation measurements. b) and c) AFM images (with same vertical scale) and linescans for nanoindents of the same tribofilm produced in lab air <12 hours after the indents were produced (green) and 27 days later (red).

To quantify the mechanical property distribution, continuous stiffness measurements (CSM) were performed with the cube corner tip on tribofilms produced in multiple environments and number of sliding cycles. Because the films had a limited thickness, a substrate effect was observed in nearly all indents, with reduced modulus and then hardness rising towards the steel substrate values with increasing indenter depth. Additionally, an indentation size effect, a surface gradient of monotonically increasing hardness and modulus near the sample surface, was observed in a majority of all indents and extended to contact depths in excess of 150 nm in most cases (see Figure 3.12b for an example). This effect cannot be explained in terms of tip
defect, as calibration indents performed on fused quartz yielded reasonable values to a contact depth as shallow as 50 nm, or as due to sample roughness, since surface roughness generally

Figure 3.9: Continuous stiffness indentation measurements using a cube corner tip with 220 Hz oscillation frequency of transfer films produced in three environments for different numbers of sliding cycles. For reference, literature indentation measurements for glassy carbon (black star) and polycrystalline graphite (black cross) are presented in (a).
results in erroneously low hardness (and modulus) in the affected contact depth range.\textsuperscript{55-57} Sample viscoplasticity can create an indentation size effect,\textsuperscript{21,58} but the exponential loading rate of the CSM indents should eliminate the effect for a purely viscoplastic response. An indentation size effect has been commonly observed in polymeric materials, with proposed explanations including an extension of the strain gradient plasticity theory to glassy materials\textsuperscript{59,60} and a surface effect based on surface energy considerations.\textsuperscript{61}

To extract reliable reduced modulus and hardness values from the mechanical property depth profiles, given the presence of the preceding effects, values were extracted only if the modulus and hardness reached a plateau between the surface and the substrate. This analysis is illustrated in Figure 3.12b. Additionally, during CSM indents a phenomenon known as the “woodpecker” effect occurred during the shallow portion of some indents, where the tip comes out of contact with the sample during the retract portion of the sinusoidal modulation. Once continuous contact was achieved, reasonable data for hardness and moduli were subsequently obtained. Nevertheless, it has been shown in the case of crystalline solids that this effect in CSM indents can lead to softening of the underlying material and underestimation of the hardness.\textsuperscript{62,63} To date, this effect has not been shown to affect the measured properties for amorphous materials. The CSM technique has been shown, however, to overestimate the hardness in some polymers due to strain rate sensitivity.\textsuperscript{64}

The distribution of mechanical properties for several tribofilms produced under multiple sliding environments and number of sliding cycles are presented in Figure 3.9a. It is evident that the films are laterally inhomogeneous, with measured hardness and modulus values ranging across three orders of magnitude. These values are lower than the as-deposited a-C:H:Si:O, which was measured to be 11 GPa by nanoindentation of a nominally identical film grown to 500 nm thickness, with a reduced modulus of 120 GPa. From all the data in Figure 3.9a, an average ratio $E^*/H$ of 9.1 was determined, which is in the typical range for a-C:H films (not tribofilms) of 6-10\textsuperscript{37,65}, and close to the $E^*/H$ of 10.9 for the as-deposited film. No statistically significant trends could be identified for variation in sliding environment or number of sliding cycles considering the very large standard deviations implied by the lateral inhomogeneity.
Figure 3.9a, for reference, also includes indentation hardness and modulus values for a commercial glassy carbon\textsuperscript{66} and polycrystalline graphite with a porosity of 15\%\textsuperscript{67} as reference compounds. These are included since prior work on tribofilms has suggested that tribofilms possess a graphitic structure. In this study, many tribofilm regions had substantially lower modulus and hardness values than these materials.

Additionally, while reliable values for the modulus and hardness are presented in Figure 3.9a, the analysis method does introduce a systematic error: the exclusion of indents from analysis in the softest regions of the films. These regions never achieved a stable reduced modulus and/or hardness prior to the substrate effect and hence reliable mechanical properties could not be determined. This effect was significant: out of the 124 indents performed, 76 indents yielded reliable moduli and hardness values. As will be shown below, indents with a blunter Berkovich tip yielded a more continuous distribution of mechanical properties down to hardnesses <100 MPa and reduced moduli <1 GPa.

One metric used to quantify the degree of viscoelasticity in a material is the loss tangent (tan δ), which is the ratio of loss modulus (modulus measured at a 90° phase lag to a cyclic stress) to storage modulus (modulus determined from in-phase strain). Tan δ = 0 for a purely elastic response while tan δ → \infty for a purely viscous response. Tan δ is generally a function of modulation frequency for viscoelastic materials. The CSM measurements determine tan δ as a function of contact depth and these results are presented in Figure 3.9b. For comparison, typical tan δ of polymethyl methacrylate (PMMA), polytetrafluoroethylene (PTFE), and rubber are, respectively, 0.1, 0.225, and 1.12.\textsuperscript{68} The results (as well as additional indents with a Berkovich tip discussed below) demonstrate that viscoelasticity is present in some regions of the tribofilm. For the particular metric of loss tangent, these values indicate substantial viscoelasticity, comparable to some polymers.

Figure 3.10 presents the moduli measurements from which the loss tangent was calculated (using a Berkovich tip in the CSM mode). These values were extracted from regions where a plateau was achieved in moduli values with depth to minimize substrate or surface influence. This data provides some context about why high loss tangents were found in softer regions.
While the storage modulus dropped three orders of magnitude across the range of hardness values, the corresponding decrease in loss modulus only ranged over little more than a single order of magnitude, leading to high loss tangents in the softest areas of the film.

Figure 3.10: Measured storage and loss moduli for two environments determined using a Berkovich tip in the CSM mode with a 220 Hz modulation. Data is presented in log-log (a) and log-linear (b) formats.

In addition to the CSM indents with a cube corner indenter, a number of CSM indents were performed with a Berkovich tip and identical indentation parameters. The distribution of hardnesses and loss tangents for transfer films formed in blowing dry air and lab air, respectively, are presented in Figure 3.11. This distribution again confirms the large degree of lateral inhomogeneity in mechanical properties. Additionally, these indents allowed for quantification of hardness in the softest areas of the films. This is reflected in the fraction of
indents that could be successfully analyzed: 86% for the Berkovich tip vs. 61% for the cube corner tip. The higher success rate is attributed to the shallower geometry of the Berkovich tip, which led to more rapidly increasing sample stiffness with indentation depth, which in turn allowed the CSM feedback to attain continuous contact and terminate the woodpecker effect at a shallower indentation depth.

![Graph showing Loss Tangent vs. Hardness for Lab Air and Blowing Dry Air](image)

**Figure 3.11:** Viscoelastic loss tangent determined using 220Hz CSM mode indents with a Berkovich tip into transfer films produced by 100 sliding cycles in lab air or 50 cycles in blowing dry air.
In addition to the CSM indents, extensive tests were also performed in the quasistatic mode. A load function with 43 unload segments, as demonstrated with the load vs. contact depth plot in Figure 3.12a, was used to determine the reduced elastic modulus and hardness at the maximum depth of each unload segment via the Oliver-Pharr method.59 The resulting depth profile allowed for the extraction of modulus and hardness values once a plateau had been reached. A plateau can be seen in Figure 3.12b for the hardness data, but not for the modulus, which is influenced by the steel substrate as well as a surface gradient, preventing extraction of a reliable value. The results from the analysis of many indents randomly distributed on the surface of a transfer film grown in each of the three different environments is presented in Figure 3.12c.

![Figure 3.12](image)

**Figure 3.12:** a) and b) Typical load-displacement curve obtained from quasistatic indentation measurements and associated series of reduced modulus and hardness values determined for each partial unload segment of the loading sequence. c) Distribution of apparent hardness measurements determined via nanoindentation for 3 ambient environments using Berkovich tip and quasistatic loading.

The distribution of hardness values show the same extreme lateral inhomogeneity discussed for CSM indents, however the lack of a woodpecker effect in the quasistatic mode allowed for
reliable quantification of the hardness in the softest regions of the film. For blowing N₂, blowing dry air, and lab air the average hardness and standard deviations of the distributions were, respectively, 300±320 MPa, 330±1000 MPa, and 1310±1450 MPa. The large errors are due to the distribution of values being very far from a normal distribution. These results suggest that transfer film formed in lab air, while still soft relative to the original a-C:H:Si:O, is predominantly harder than the transfer films formed in the other environments.

Hardness values are plotted instead of reduced modulus in Figure 3.12c, as a greater fraction of the total indents could be successfully analyzed, but where modulus could be quantified, a similar spread in values was observed, ranging from <100 MPa to 60 GPa. This is shown in Figure 3.13 for the same data set. The ratio E*/H determined from this data (excluding the high outlier from the blowing dry air transfer film) was 7.7. This value is close to the E*/H of 9.1 determined from the CSM indents performed with the cube corner indenter.

![Figure 3.13: Mechanical properties determined by quasistatic Berkovich nanoindentation for several environments.](image-url)
Tribofilm Spectroscopic Characterization

Tribofilms grown in the three environments were examined using SEM and EDX. The results of immediately sequential measurements with identical imaging parameters are presented in Figure 3.14. The top row shows secondary electron images of the three tribofilms. The morphology is characteristic for each environment. Tribofilms grown in ambient air were generally continuous, whereas those grown in blowing dry air or blowing N\textsubscript{2} were patchier, with their thickest and most continuous regions along the edge of the contact zone. The EDX maps demonstrate that there are substantial compositional differences between tribofilms grown in the three environments. All of the measurable constituents (Si, O, C) of the original a-C:H:Si:O are transferred to the counterface. Carbon is present in much larger amounts for the inert blowing dry N\textsubscript{2} case, with decreasing carbon in the ambient air case, and less still in the case of blowing dry air. Silicon and oxygen are much more abundant in the reactive environments than in blowing N\textsubscript{2}. Additionally, there appears to be enhanced lateral inhomogeneity in the distribution of Si and O for the blowing N\textsubscript{2} case.
To explain the varying abundance of carbon in the three films, we propose that environmental species such as water vapor and oxygen etch carbon prior to and/or after adhesive transfer to the tribofilm. Oxidative stress selectively attacks carbon in defective...

Figure 3.14: SEM/EDX mapping of PIII D a-C:H:Si:O transfer films formed in three different environments. Each column is a single tribofilm, with each row showing a different analysis, in order: secondary electron image, EDX of carbon Kα, silicon Kα, and oxygen Kα X-rays.
configurations with dangling bonds as well as sp$^2$ carbon more readily than sp$^3$,$^{70,71}$ and mechanical stress is known to reduce the activation energy required for chemical reactions including oxidation, i.e. mechanochemistry.$^{72,73}$

Raman spectroscopy was also performed on tribofilms grown in each of the three environments. The as-deposited a-C:H:Si:O film, as well as each tribofilm, showed the characteristic D and G peaks of sp$^2$ bonding in DLCs. Raman spectroscopy was performed at several positions on each tribofilm. The spectral features were repeatable across each tribofilm surface despite the lateral inhomogeneity observed in EDX. This is attributed to the limited lateral resolution of the confocal Raman, which is often equated with the laser spot size on the sample (~1 µm), but can be degraded in transparent samples.$^{74}$ Representative spectra are presented in Figure 3.15. The as-deposited PIII a-C:H:Si:O spectrum is included for reference. The poor signal-to-noise ratio for the as-deposited spectrum is a consequence of its small thickness of 40 nm, as compared to the tribofilms, which were all >500 nm thick. The as-deposited spectrum is typical of an amorphous carbon, with a convoluted G-peak and a D-peak that can only be resolved through peak-fitting. Both features arise from sp$^2$ bonding, as the scattering cross section of π states is more than 50x larger than the cross section for σ states for visible wavelength photons.$^{75,76}$ The G peak is due to stretching of sp$^2$ C-C bonds and the D peak is due to the breathing mode of 6-fold sp$^2$ carbon rings. The spectra from the tribofilms are very different, both from the as-deposited film, and from each other.
The as-deposited film could be fit with 2 Gaussian peaks, with G-peak at 1455 cm\(^{-1}\) and \(I_0/I_G = 0.18\). The blowing dry air and blowing N\(_2\) tribofilm spectra are each composed of 4 peaks, 2 of which are assigned as G and D, based on their prominence in the lab air tribofilm. Relative to the as-deposited sample, the photoluminescence background, which is apparent as the overall slope of the spectrum relative to the intensity of the G peak, increases substantially, especially for the tribofilms grown in the environments deficient in water vapor. This effect can be due to passivation of carbon dangling bonds by hydrogen and clustering of the sp\(^2\) phase.\(^{77,78}\) In a-C:H materials, the shift of the G peak to higher values in the tribofilms is consistent with clustering of the sp\(^2\) into rings at the expense of long olefinic carbon chains.\(^{75,77}\) In the three stage model of

![Raman spectrum diagram]

**Figure 3.15:** 532 nm Raman spectra for the PIII-D-grown a-C:H:Si:O and transfer films produced in 3 ambient environments during macroscale tribometer experiments that differed only in the number of cycles performed.
disordered carbon evolution, these changes are also consistent with an increase in the sp² fraction of the film. The large photoluminescent background and additional peaks in the relevant spectral range prevented accurate fitting of the D and G peaks of the tribofilms formed in blowing N₂ and dry air. Fitting of the lab air tribofilm revealed \( I_D/I_G = 0.95 \) (or 0.97 if fit with four peaks). The increase in \( I_D/I_G \) unambiguously indicates an increase in clustering of the sp² phase, at least for clusters of a particular distribution of size and shape probed by the 532 nm laser used here. The additional tribofilm peaks at 1430 and 1620 cm⁻¹ along with several additional peaks between 1100 and 1800 cm⁻¹ cannot be assigned with confidence. Possibilities include the influence of a polymeric structure which can result in several additional peaks between 1000-2000 cm⁻¹, and the 2nd order transverse optical and longitudinal vibrations of Si-C bonds, which can be found in this region for some SiC allotropes.

To further clarify the tribofilm structure, a cross section of a tribofilm spanning four indents was produced with Ga⁺ focused ion beam milling for TEM imaging. Figure 3.16 shows two intermediate conditions during the FIB cross-sectioning process for a tribofilm grown during 500 cycles of sliding in a blowing N₂ environment. These images demonstrate how the cross-section

![Figure 3.16](image-url)
location was chosen to allow for a comparison between local morphology and mechanical properties determined via nanoindentation.
Figure 3.17: a-d, top row: HAADF images of four regions where nanoindents were performed prior to cross sectioning of the tribofilm produced after 500 cycles of sliding in a blowing N₂ environment. a-d, bottom row: EELS composition maps for the same four regions. Si mapping omitted for clarity since O/Si regions fully overlapped e: EELS low loss spectra for carbon-rich areas of each of the four regions. f: Representative carbon K-edge spectra for the tribofilm and an AFM probe coated with the unmodified a-C:H:Si:O.
High angle annular dark field (HAADF) images of the regions where four indents (with substantially varying measured hardness and modulus) were performed are displayed in Figure 3.17a-d. The image contrast in different regions of the cross sections varies considerably, indicating lateral variation in composition and/or density. A few voids are also observed in the cross section (e.g. spot 3, Figure 3.20), though they are not numerous and therefore unlikely to explain the degree of lateral inhomogeneity observed in the mechanical properties. The bottom row Figure 3.17a-d shows EELS elemental mapping of the same regions. Wherever the O-K edge is detected the Si-L edge is also present; Si maps are shown in Figure 3.18. The most striking feature in Figure 3.17 is that the Si/O and C have largely segregated in regions 1-3, with SiOₓ areas and carbon-rich, presumably CHₓ, areas. One possible way to explain this would be selective transfer from a similarly segregated as-deposited a-C:H:Si:O film. However, all spectroscopic evidence, including similar EELS maps from an AFM probe coated with a nominally identical a-C:H:Si:O film as shown in Figure 3.19, indicate that the as-deposited a-C:H:Si:O is compositionally homogenous. This suggests that tribological stress provides a driving force for mass transport which leads to the thermodynamically favored bonding of the Si to O and carbon to other carbon and hydrogen across lengthscales spanning at least hundreds of nm. This remarkable transformation provides a reasonable explanation for some of the inhomogeneity observed, with the tribofilm composed of compositionally homogenized regions along with regions displaying various degrees of compositional segregation.
In addition to the composition maps, individual summed EELS spectra from the carbon-rich regions were analyzed to determine changes occurring to the bonding configuration of carbon atoms in the tribofilm. Figure 3.17f shows a set of low loss spectra obtained from the four transfer film regions. The intensity of the $\pi^*$ plasmon around 7 eV is an indicator of the degree of ordering in the carbon sp² phase into ring structures, whether isolated as in benzene or polystyrene or forming extended structures as in graphite. It is clear that the degree of ordering of the sp² phase varies between different regions, with regions 2 & 3 showing substantial ordering and regions 1 & 4 showing no such indications of ring structures. In all
cases, the degree of ordering is less than in a graphitic material like lacey carbon, which is also shown for reference.

![Figure 3.19: HAADF (left) and EELS composition map (right) of a Si AFM probe which has been coated with a-C:H:Si:O in a nominally identical deposition to the one used to prepare the flat samples subjected to tribometry.]

Because the carbon K-edge spectra from the tribofilms did not possess clearly resolved C1s→π* peaks which could be used as an internal loss energy reference, quantification of the sp³ fraction of the tribofilms could not be performed. Nevertheless, some useful qualitative observations could be made via comparison to C-K spectra from an AFM probe coated with a nominally identical a-C:H:Si:O to that used to produce the tribofilms. The spectra were aligned based on the assumption that the degree of sp² bond length and angle disorder were similar between the tribofilms and a-C:H:Si:O, and so the pre-edge of the C1s→π* peaks could be aligned. The maximum of the a-C:H:Si:O C1s→π* peak was placed at 285.0 eV to agree with other studies of disordered carbon materials. Finally, the overall intensity of the spectra were normalized to have matching maximum C1s→(π+σ)* intensities, rather than the more typical and informative post-edge normalization to the intensity at some loss energy value above 310 eV. This choice was made since it was found for the relatively thick films analyzed here that the plural scattering correction did not provide similar post-edge intensities for different local
thicknesses and hence post-edge normalized intensities would not provide meaningful comparisons of relative intensity at equivalent loss energies. Despite these caveats, the spectra provide some clear comparative observations. While the lack of an obvious increase in the intensity of the C1s→π* peak might suggest that any increase in the sp² fraction of the tribofilm relative to the unmodified a-C:H:Si:O is modest, it is also possible that ordered sp² carbon is produced, which would be centered at 285.5 eV (rather than 285.0 eV) and hence broaden the peak rather than increase its height. It is clearly evident that there is a large increase in the relative intensity around 287–288 eV, which cannot be explained with broadening of the C1s→π* peak, and which is consistent with a substantial increase in the C-H bonding in the tribofilm, as was recently seen in another a-C:H:Si:O tribofilm study. The increase in C-H bonding is large enough to obscure the position of the C1s→π* peak. As well, since the C-K spectra from the different tribofilm regions were visually indistinguishable, this indicates there is a substantial increase in C-H bonding for all regions of the tribofilm.

No correlation between EELS results and the mechanical properties determined from the indents could be identified. Hardness values for the four indents in this region ranged from 0.5 – 1.6 GPa as shown in Table 3.1. While the degree of ordering of the sp² carbon did clearly rise in the vicinity of the indents with the lowest hardnesses and moduli, the variation in compositional homogeneity could equally rationalize the differences measured.

<table>
<thead>
<tr>
<th>Hardness (MPa)</th>
<th>Reduced Modulus (GPa)</th>
<th>Loss Tangent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Indent #1</td>
<td>1190</td>
<td>18</td>
</tr>
<tr>
<td>Indent #2</td>
<td>960</td>
<td>17</td>
</tr>
<tr>
<td>Indent #3</td>
<td>540</td>
<td>11</td>
</tr>
<tr>
<td>Indent #4</td>
<td>1630</td>
<td></td>
</tr>
</tbody>
</table>

Table 3.1

Several images at a magnification sufficiently high to attain atomic lattice resolution were also analyzed (Figure 3.20). These images showed a predominantly amorphous morphology. Two small crystallites embedded in the amorphous structure were observed. Fast Fourier transforms (FFT) of the high resolution images confirmed the primarily amorphous structure,
but faint spots corresponding to lattice spacings of 0.224±0.005 and 0.190±0.005 nm were observed in multiple images. The 0.224 nm spacing is due to contamination of the cross section faces with Pt from the milling process, which has a lattice spacing 0.226 nm for the \{111\} family of crystal planes. The 0.190 nm spacing could be attributed to the visible crystallites in the image by measuring the spacing in the real space images, but their composition and structure could not be identified.

![Figure 3.20: TEM images demonstrating the location of four indentation performed prior to the cross-sectioning process. Red circles indicate the position of high resolution images and associated FFTs in the lower panels.](image)

**Discussion**

This study presents a collection of results focused on the post-sliding characterization of a-C:H:Si:O tribofilms, motivated by tribometry data indicating that the presence of tribofilm is critical to achieving low friction in this system. The spectroscopic characterization of the tribofilms shows that the composition and structure vary considerably depending on the sliding environment. In the inert blowing N₂ environment, EDX demonstrates that the tribofilm is rich in
carbon, with the tribofilm becoming relatively richer in silicon and oxygen as oxygen and water vapor are added to the sliding environment. This change in composition is attributed to chemical etching of carbon during sliding due to environmental species, either during the adhesive transfer process or from within the tribofilm. Water vapor appears to limit the rate of etching, as the humid air tribofilm was richer in carbon than the tribofilm grown in dry air. Raman spectroscopy also shows durable differences in the structure of the tribofilms produced in the different environments.

The mechanical characterization of the tribofilms with nanoindentation indicates that the films are much softer than the original a-C:H:Si:O. However, the extreme softness of many regions of the tribofilms, with hardness values below 100 MPa and reduced modulus values below 1 GPa, along with a viscous mechanical response, strongly suggest that the tribofilms possess a polymeric structure. Several other observations support this conclusion as well, including the transparency of the tribofilms, hysteresis in the quasistatic indentation load vs. depth plots, the indentation size effect, and the indent depth recovery over time. Other studies of DLC and diamond tribofilms provide some additional support for this proposition. Secondary ion mass spectrometry of DLCs has shown that hydrocarbon macromolecules or aliphatic fragments are present in the wear track or tribofilm that are not present in the original DLC. Nanoindentation and dynamic AFM have also demonstrated a reduction in hardness or modulus of worn DLC material, though not clearly of a magnitude that rules out a primarily graphitic structure.

Raman data consistent with an ordering transition relative to the original a-C:H:Si:O and implying an enrichment of sp² carbon must be reconciled with interferometry measurements indicating the tribofilms are partially transparent. Optical transparency is expected of a prototypical long chain carbon-based polymer which is highly sp³ bonded, whereas a high density of sp² carbon is associated with high electrical conductivity and therefore opaque materials. We propose that chemistry modulates the structure of the tribofilms, with broken carbon bonds being passivated with environmental or dopant species and leading to the formation of polymeric sp³ chains. Even in the nominally inert environments of blowing dry air or N₂, the partial pressures of water vapor and O₂ remain higher than the minimum threshold
shown to chemically modulate the friction in ultrahigh vacuum studies of other a-C:H:Si:O. Simultaneously, the remaining $sp^2$ carbon fraction of the film can evolve under tribological stress consisted with the Ferrari model, i.e. toward more ordering of the $sp^2$ phase in the films. Hence, there is no inherent contradiction between the transparency suggested by the interferometry and the Raman results indicating ordering of $sp^2$ carbon-carbon bonds.

The proposed polymeric structure is also in disagreement with a sizable literature characterizing the structure of DLC tribofilms and wear tracks as “graphitic.” In many cases (e.g. Refs 4,12–14,39), this determination is made based on an increase in the intensity of the Raman D-peak relative to the Raman G-peak under the framework of the Ferrari 3-stage analysis of amorphous carbon Raman spectra, though the original papers proposing a wear-induced graphitization model of lubrication offer additional TEM diffraction data supporting domains of crystalline graphite as evidence. As previously discussed, changes which are fully consistent with the Ferrari model of the ordering trajectory of a-C:H are found here as well. Namely, these consist of an upshift in the G-peak position, an increase of the ratio $I_D/I_G$, and an increase in the photoluminescence. While these changes indicate ordering consistent with the Ferrari model, in this case it does not necessarily indicate ordering has progressed to the formation of domains of crystalline graphite, and indeed, none could be identified in TEM imaging. The presence of graphitic domains would manifest as spots or rings at lattice spacings of 0.142 or 0.335 nm in the FFT’s of high-resolution images. Researchers have often suggested that easy shear of graphite sheets formed in the wear process could be important for the low friction observed in various carbon-based solid lubricants, and have presented some evidence for the presence of graphitic domains in the tribofilms. One study convincingly demonstrates that graphite is absent from the wear tracks of a ta-C film worn under several conditions of load and environment, but the same conclusion could not be drawn about the counterface tribofilm. The TEM results here indicate that $sp^2$-bonded carbon domains with long range order are not present in any significant concentration in the bulk of the tribofilm, although graphitization in the near-surface region of the tribofilm cannot be ruled out. Low loss EELS spectra also indicate that the degree of ordering of the $sp^2$ phase into rings varies across the tribofilm, with some regions showing no sign of significant ordering.
The EELS compositional mapping performed for a tribofilm grown in blowing N\textsubscript{2} provide a partial explanation for extreme lateral inhomogeneity in mechanical properties. There is a progressive segregation of the Si/O and C in the tribofilm, and regions with different degrees of chemical segregation could be expected to possess very different mechanical properties. Additionally, the distribution of mechanical properties determined from quasistatic indents and CSM indents with a Berkovich tip indicate that tribofilms produced in blowing dry air or N\textsubscript{2} have smaller average \(E^*\) and H. These differences, however, cannot be used to explain the variation seen in friction for the different environments. Researchers have demonstrated repeatedly that DLCs can show abrupt and reversible friction changes when the environment is also changed abruptly.\textsuperscript{34–36} We performed similar tests on the PIIIID a-C:H:Si:O by turning the flow of blowing N\textsubscript{2} on and off and found the same behavior. The change in friction is abrupt and reversible and therefore deemed unlikely to be due to any changes in the mechanical properties of the bulk of the tribofilm. A similar argument can be made for wear results as well. While wear was not examined in detail for this paper, the predominantly soft tribofilms grown in blowing dry air clearly resulted in the highest a-C:H:Si:O wear rate, with the 40 nm film wearing out in as few as 100 cycles, as compared to 2000 cycles for the similarly soft tribofilms grown in blowing N\textsubscript{2}.

There is structural diversity present both within a single tribofilm, as demonstrated by the varying degree of compositional segregation in the EELS results (Figure 3.17), and between tribofilms, as shown in the EDX of tribofilms grown in different environment (Figure 3.14). This provides some insight about the lubricity of the tribofilms. The SiO\textsubscript{x}-rich tribofilm grown in dry air provides similar lubrication to the relatively carbon-rich tribofilm grown in dry N\textsubscript{2}. EELS demonstrates that SiO\textsubscript{x} segregates from the carbon in the tribofilms such that some regions of the tribofilm are dominated by SiO\textsubscript{x} and have undetectable fractions of C. The fact that these carbon-free regions do not adversely affect the overall friction, even in the dry air case where SiO\textsubscript{x} is expected to be the dominant phase, raises the question as to whether graphitic carbon domains are necessary to achieve low friction, and if the presence of carbon at all is necessary. A polymeric structure to limit high stresses at asperity contacts, which could remove passivating species, along with well-passivated surface bonds, may be the primary requirements for low friction against a similarly passivated a-C:H:Si:O wear track. In Chapter 4, evidence will be presented which suggests that physical pinning (rather than interfacial bonding) dominates
friction even in the case of hard asperity contacts. In such a case, the softness of the tribofilms shown in this chapter might be crucial in allowing for easy depinning of the interface, thereby lowering friction.

The extreme softness and viscoelasticity of some regions of the tribofilms grown in blowing N\textsubscript{2} provide a plausible explanation for the growth in the width of the wear track beyond the nominal Hertzian radius (Figure 3.1b). Many areas of these tribofilms showed hardness values below the nominal Hertzian pressure, and thus the tribofilm could have been squeezed out of the initial contact zone, aided by viscous flow, causing the nominal contact area to grow. Additionally, these results could provide a rationalization for why non-Amontonian behavior is observed in some DLCs (and other solid lubricants), where the friction coefficient depends on the applied load\textsuperscript{90,91} Some success has been achieved in calculating the interfacial shear strength by modeling the real contact area with Hertzian contact mechanics.\textsuperscript{12} A reduction in the effective modulus of the counterface due to the tribofilm reduces the critical load required to achieve Hertzian friction scaling.\textsuperscript{92}

Additionally, there is also a striking correlation between the loss tangent, measured hardness, and the reduced modulus. We hypothesize that as regions of the tribofilms become increasingly polymeric (whether the SiO\textsubscript{x}- or carbon-rich regions), the reduction in bonding between neighboring polymeric chains reduces both the hardness and modulus, and simultaneously endows the film with viscoelastic properties. In the simplest model of elastomer deformation, the modulus is inversely proportional to the chain length between crosslinks.\textsuperscript{93} A similar dynamic could be occurring in these tribofilms. Under the influence of the cyclic tribological stress in the bulk of the tribofilm, strained crosslinks are progressively broken, with the resulting dangling bonds saturated by environmental constituents leading to long chains of sp\textsuperscript{3} carbon and a polymeric film.

**Conclusions**

In this study, a PIIIID-grown a-C:H:Si:O with a high Si concentration was tested with ball on disk friction experiments in various environments. Low friction coefficients with a modest
sensitivity to humidity and no sensitivity to oxygen were observed. Additionally, sliding of a tribofilm against a bare Si substrate led to an extended period of low friction prior to wearing out of the tribofilm, implying a high inherent lubricity of the tribofilm.

Characterization was performed on tribofilms produced in multiple environments. This characterization showed that the composition and structure of the films varied depending on the sliding environment in which it was produced, as demonstrated in EDX and Raman results. The concentration of carbon in the films was reduced when abundant H₂O and/or O₂ were present in the environment, suggesting oxidation and volatilization of carbon at the sliding interface as an explanation. In all cases, Raman spectra showed a substantial increase in sp² clustering in the tribofilms relative to the original a-C:H:Si:O. The extreme thickness of the tribofilms allowed for nanoindentation analysis, which showed that the tribofilms were substantially softer than the original a-C:H:Si:O and were laterally inhomogeneous in their mechanical properties. Additionally, a viscous mechanical response was measured in softer regions of the film. The lateral inhomogeneity was rationalized as due, in part, to a dramatic segregation of Si/O from carbon in some regions of the transfer film. The extreme softness and viscoelasticity of many regions of the film suggest a polymeric structure for the tribofilm, rather than a graphitic or sp²-rich fully amorphous a-C:H:Si:O structure. EELS results indicating an enrichment in C-H bonding of the film are consistent with a polymeric film structure. Direct TEM imaging of a tribofilm cross section as well as EELS low loss spectra provide further evidence that a graphitic structure does not explain the mechanical properties of these films.

References


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CHAPTER 4 – Nanoscale Tribological Response of a-C:H:Si:O

Introduction

While DLCs have been extensively studied spectroscopically and in macroscale tribological experiments, nanoscale studies with atomic force microscopy (AFM) are relatively less numerous. AFM has often been used to characterize the friction and topography of as-deposited DLC films. These studies intentionally utilized low loads to minimize sample wear. However, it is known that the DLC surface is substantially modified during the run-in process at the macroscale, and during this process the friction coefficient generally decreases substantially as a tribofilm tends to build up on the contacting surfaces. The present study is an attempt to recreate these conditions at nanoscale and understand the transformations which occur. There is some limited precedent for this type of work. Wear studies using AFM have been performed several times. Sliding a large radius (>100 nm) tungsten tip on amorphous carbon (a-C) showed that wear rates are accelerated in the presence of water vapor and reduced in the presence of substantial hydrogen, a result in agreement with macroscale trends. Sharp Si₃N₄ AFM tips have been slid on a-C across meters of sliding distance and showed a modest reduction in friction, but the experimental conditions were not specified in enough detail to determine if it was changes in the a-C or the AFM tip that were probed. Additionally, several additional AFM wear studies on DLC have been performed, though in some cases the wear rate was influenced by extremely small film thicknesses.

This study examines the evolution of nanoscale friction as a function of load and sliding cycles, making use of an underutilized but powerful technique which can quantify the contact area as a function of load, thereby allowing the interfacial shear strength of the sliding contact to be continuously monitored during the sliding experiment.

Experimental Methods:

AFM sliding experiments were performed using two instruments. The first was an Asylum MFP-3D (Asylum Research, Santa Barbara, CA) where experiments were performed in ambient lab air.
The other instrument was an RHK 350 (RHK Technology Inc., Troy, MI) using an RHK R9 controller. This microscope was mounted in a vacuum chamber with constantly flowing gas and hygrometer monitoring for environmental control. Dry environments were attained by flowing N₂ boiled off from a liquid nitrogen dewar through the chamber until hygrometer readings were stable at 0.0% RH before commencing experiments. Humid environments were attained by bubbling a fraction of the flowing N₂ through deionized water. The humidity meter (Fisher Scientific, Pittsburgh, PA) was calibrated to an accuracy of ±1.0 %RH.

Two types of contact mode AFM probes were utilized for this study: contDLC (Budget Sensors, Sofia, Bulgaria) ta-C-coated silicon probes, and AD-I-0.5-AS (Adama Innovations Ltd., Dublin, Ireland) single-crystal diamond-coated silicon probes. It was expected that such hard probes would experience much less wear and chemical modification than the a-C:H:Si:O sample, thereby allowing experiments to reveal changes to the a-C:H:Si:O rather than the probes. Normal forces were calibrated using the Sader method in air.¹³ Lateral forces were calibrated using either the wedge¹⁴ or diamagnetic¹⁵ lateral force calibration method.

The a-C:H:Si:O used in this study was grown from a hexamethyldisiloxane precursor using plasma immersion and ion implantation deposition by NCD Technologies, LLC. and is the same material discussed in Chapter 2. The bulk composition of the a-C:H:Si:O was 26±10 at.% carbon, 11±5 at.% silicon, 15±4 at.% oxygen, 47±4 at.% hydrogen with an sp³ fraction of 73±3 at.%. The silicon wafer used for sliding experiments was [100] oriented, n-type, polished and etched (El-Cat, Ridgefield Park, NJ). HOPG (Ted Pella, Inc., Redding, CA) was exfoliated with scotch tape immediately prior to sliding experiments. The a-C:H used in this study was obtained from HGST, San Jose, CA, and has been described previously.¹⁶ These films were doped with 26±3% hydrogen and had a carbon sp³ fraction of 47±4 at.%. Bulk mechanical properties used in the calculation of lateral contact stiffness were, for ta-C: 337 GPa shear modulus¹⁷ and 0.17 Poisson ratio.¹⁸ For the a-C:H:Si:O, it was assumed the ratio of shear to Young’s moduli was 0.38¹⁷ so a shear modulus of 46 GPa could be determined from the nanoindentation Young’s modulus of 120 GPa (see Chapter 3). The same Poisson’s ratio was used for a-C:H:Si:O as for ta-C. The shear modulus and Poisson’s ratio used for diamond were, respectively, 478 GPa and 0.1.¹⁹
Results

Figure 4.1 shows the friction dependence on load for a ta-C-coated AFM probe sliding on three different materials in a humid environment (50±1%RH). Each measurement was started at a load of 50 nN, and then the load was decremented every scan line. The data were acquired in imaging mode, where the image size in the slow scan direction (AFM images are formed via a raster scanning pattern, “slow scan” refers to the direction of sequential scan lines in this pattern) was chosen to be large enough, given the tip radius (estimated to be 20 nm by blind tip reconstruction of a topographic image of an ultrananocrystalline diamond sample), to ensure there was no overlap of sequential scan lines, thus avoiding any changes that may accrue due to wear of the substrate. The measurements were repeated in a randomized order to ensure the trends were robust against possible tip geometry and structural changes. It is immediately apparent that friction on the as-deposited a-C:H:Si:O is very high across the entire load range relative to highly oriented pyrolytic graphite (HOPG), and is quite similar to the result for silicon. It is also clear from the magnitude of the pull-off forces, that despite the more than an order of magnitude difference in friction between HOPG and the other materials, the adhesion forces are similar. Thus, lower adhesion between the tip and the graphite is not the
source of its lower friction. It also raises questions about the inherent lubricity of the as-deposited a-C:H:Si:O film given that it performs similarly to silicon (or SiO, since a native oxide will always be present), which is, in general, a very poor solid lubricant at macro- and microscale.\textsuperscript{21,22} Of course, numerous other effects come into play at larger length scales e.g. wear particle abrasion that can be absent at nanoscale.

It should also be mentioned that similar experiments were performed with Si probes as part of this study and were in qualitative agreement with the result in Figure 4.1, but the use of these probes was abandoned in favor of the much harder and more wear resistant ta-C-coated probes due to an unacceptably high rate of adhesive transfer from the Si tip to the a-C:H:Si:O. This is illustrated in Figure 4.2 where >10 nm of Si could be transferred to the wear track in several hundred cycles of sliding the AFM tip over the same region. ta-C coated probes provided a much more stable tip geometry for this test and especially the ones to follow, where a stable tip geometry is crucial to the analysis.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure4.2.png}
\caption{Topographic image and associated linescan of worn surface of a-C:H:Si:O after sliding a silicon AFM tip at 200 nN applied normal force across 500 nm with slow scan disabled for 256 cycles in 47±1%RH air. A large volume of silicon which has been transferred from the AFM tip to the wear track is observed. The characteristic triangular shape seen in the image is an artifact due to the fact that the tip has been blunted by this material removal, and its remaining triangular-shaped base is obtaining the image.}
\end{figure}

In order to examine the surface transformation of a-C:H:Si:O under repeated sliding, the slow scan direction was disabled in the AFM so all scan lines were nominally over the same region, to the extent permitted by thermal drift. Figure 4.3 shows the resulting friction as a
function of sliding cycles for two different tip materials, ta-C and single crystal diamond (sc-d).

Figure 4.3: Friction trends at various loads for (a) & (b) ta-C coated and (b) diamond-coated AFM probes for reciprocating sliding across 2.4 µm on previously unworn a-C:H:Si:O. Trials are numbered chronologically. The horizontal arrow in (a) is a guide to the eye. Every trial was performed on previously unworn a-C:H:Si:O.
Every trace was performed starting on previously-unworn a-C:H:Si:O. Above some threshold load, it is clear that the friction can drop substantially, in a manner qualitatively similar to what is observed during macroscale run-in of DLC’s\textsuperscript{23,24} and for this a-C:H:Si:O film. Moreover, it is conclusively demonstrated that these friction changes are due to changes to the a-C:H:Si:O sample rather than the tip, given that in all cases, the behavior was immediately repeatable on an unworn area of a-C:H:Si:O. It is unclear why the friction decayed more slowly for the blunter ta-C tip compared to the two sharper tips, but potentially it is related to the much larger radius of this ta-C probe. Similarly, the threshold load to achieve a measurable friction drop was higher for the blunter probe. The blunter probe will lead to higher adhesion but lower contact stresses, thus reducing the rate of stress-activated processes. A more detailed investigation of the effect of tip radius was not undertaken as the tip radius of these commercial probes could not be easily controlled and were typically in a narrow range between 10 and 30 nm. Additionally, across longer timescales than those above, as will be shown later, the structure of the ta-C AFM tips changes and modifies the friction, so wearing of the tips to produce larger radii would lead to additional tip changes.

Figure 4.4: Bright field TEM imaging of (a) the blunt ta-C coated AFM probe used for the testing in Figure 4.3a after completion of sliding tests and (b) a different, new ta-C coated AFM probe with a smaller apex radius.
The larger radius of ta-C probe in Figure 4.3a was also believed to play a role in the lack of repeatability when reducing the load at the end of the tests from 800 to 400 nN. In this case, the friction was not comparable to the previous trials at the same load (compare to Figure 4.3c where the friction response was repeatable in the final tests at 20 and 100 nN). This is attributed to the formation of a transfer film during the first test at 800 nN. In that case, the friction trend was not immediately repeatable, in fact, the friction in the second 800 nN trial started where the previous 800 nN test ended, as indicated by the grey arrow. This must be due to a change of the AFM tip. Likewise, the much lower friction during the 2nd set of trials at 400 nN (Trial #7 and #8) is indicative that a tip change continued to control the friction. The friction reduction in Trial #7 and #8 was also accompanied by a reduction in adhesion from 247 nN to 23 nN. The formation of a transfer film is the most likely explanation for the changes observed, and subsequent TEM imaging of the probe showed an amorphous deposit in the contact region as shown in Figure 4.4, but without pre-sliding TEM images, this deposit could not be conclusively identified as distinct from the ta-C coating.

To further illustrate the transformation occurring on the a-C:H:Si:O sample surface, a set of friction trials with a progressively decreasing load in presented in Figure 4.5. The traces with
the slow scan enabled show an approximately linear decrease in friction with decreasing load for sliding on unworn material. This is typical behavior for a stable multi-asperity contact. For the trials with the slow scan disabled, the friction quickly drops before achieving approximately linear behavior, indicating the modified surface of the sample achieves a new, lower friction coefficient (to the degree that the concept of a friction coefficient is valid at nanoscale) thanks to the repeated scanning over the same line.

To determine the load dependence of friction on the modified surface (as opposed to while modifying the surface), a modified region was created by repeatedly sliding a ta-C probe at high load (400 nN) over a region in a direction parallel to the cantilever axis, then measuring the load-dependent friction across a region encompassing this modified area. In this way, the load-dependent friction behavior of modified and unmodified a-C:H:Si:O could be directly compared. The results in Figure 4.6 demonstrate that the friction is reduced by 0-17% in the worn region, with the difference apparent for loads between ~40-300 nN. One interesting
phenomenon that was observed was that friction was slightly higher on the modified region at the lowest loads (below 15 nN).

Figure 4.6: a) Friction image on a-C:H:Si:O in 50±1%RH air with the normal load increased by 0.8 nN after each scan line. In the center of the image is a preworn region produced by repetitively scanning the same line 256 times at 400 nN normal load. b) Average friction across unworn region and linescan through preworn region of the image area. The abrupt change in the worn region friction at 315 nN is due to the worn region not extending across the entire image.
After this measurement was conducted, a 5x5 \( \mu m^2 \) area was imaged at zero applied load, which contained the 2x2 \( \mu m^2 \) region scanned in Figure 4.6. Measurable wear of the a-C:H:Si:O was observed, with a wear depth of 0.6 nm in the vertical stripe region (the region that was pre-worn before acquiring Figure 4.6), and lesser, load-dependent wear of 0-0.5 nm depth that occurred during the acquisition of the friction measurement shown in Figure 4.6. This is shown in Figure 4.7 along with friction measurements further demonstrating how the wear of the surface in ambient air leads to a new surface that exhibits an increase in friction of 0-70% at the lowest loads.

![Image](image_url)

**Figure 4.7:** Friction (a),(c) and height (b),(d) image and linescans of region in Fig. 4, post-wear, performed at 0 nN applied normal load. Linescans are taken from bottom to top of the images. There is appreciable wear and the friction is high relative to the unworn region. Friction is higher in the worn region due to the non-monotonic change in the shear strength with applied load when sliding in humid air.

**Interfacial Shear Strength Measurement**

Given that the sliding-induced changes to the a-C:H:Si:O highlighted so far indicate a change in the interfacial shear strength, an AFM-based technique for measuring the interfacial shear strength of the sliding contact was implemented. The technique is based on the fact that
the lateral stiffness of a contact in the elastic continuum case is rigorously proportional to the real area of contact:

\[ K_C = 8 G^* a \]  

(1)

where \( K_C \) is the lateral stiffness, \( G^* \) is the reduced shear modulus of the contact, and \( "a" \) is the real area of contact. Once the contact area as a function of load is determined, it is straightforward to calculate the interfacial shear strength from experimentally-determined friction forces.

The lateral stiffness of the contact can be measured in AFM by applying a small lateral oscillation to the cantilever and measuring the lateral force response using a lock-in amplifier as a function of the normal load. A requirement for the validity of the measurement is that the tip cannot slip on the sample surface. However, such slipping is accompanied by dissipation and manifests as a change in the phase of the lock-in signal, which was monitored during the measurements. In the case of AFM, since the measured stiffness is due to both the deformation of the contact and torsional bending of the cantilever, in series, the measured stiffness is:

\[ K_{Total} = \left[ \frac{1}{K_L} + \frac{1}{K_C} \right]^{-1} = \left[ K_L + \frac{1}{8 G^* a} \right]^{-1} = \left[ \frac{1}{K_L} + \frac{1}{8 G^* \left[ \frac{3 R}{4E^* (L + L_C)} \right]^{1/3}} \right]^{-1} = \left[ \frac{1}{K_L} + \frac{1}{C(L + L_C)^{1/3}} \right]^{-1} \]  

(2)

where \( K_L \) is the torsional stiffness of the cantilever. The real contact area is then substituted for the Derjaguin, Muller and Toporov (DMT) model\(^2^7\) for the real contact area with \( R \) the reduced radius of the contact, \( E^* \) the reduced modulus of the contact, and \( L_C \) the pull-off force of the AFM tip. The final expression demonstrates the free parameters that must be fit to the experimental lateral stiffness data (\( K_C \), \( C \), and \( L_C \)). This measurement method is demonstrated in Figure 4.8(a), where it is seen that the lateral stiffness data as a function of load can be extremely well-fit by this model. One complication to this approach is that it is now known that at the nanoscale, for single asperity tips, continuum mechanics breaks down to some degree due to the atomistic structure of the interface and due to compliance across the interface.
This is relevant to this measurement because it leads to significant errors when

Figure 4.8: Tests with single crystal diamond probe (tip radius = 14 nm) sliding
on a-C:H:Si:O in 26 %RH air. (a) Stiffness data and fit from the lateral force
lock-in response to a ±1.8 nm, 2 kHz modulation in the lateral direction. b) Friction vs. normal load, slow scan disabled, 200 nm scan length, 512 scan
cycles per image, normal force incremented ± 0.08 nN per cycle, repeated once (2nd image is hashed trace). c) Shear strength calculated from data in (b).
The rainbow color scheme of the traces follows the measurement, with red at
tip pull-in, then green, blue, and finally violet at pull-off.
assuming the continuum lateral stiffness expression $8G* a$ is accurate when using the bulk shear modulus. Ref. 28 suggests that an effective shear modulus much smaller than the bulk modulus can be effective in accurately modeling the lateral contact stiffness, if an appropriate effective modulus can be found.

Here, we have chosen to calculate an effective $G*$ by assuming the validity of the DMT model at this scale and calculating $G*$ from the experimental fit parameter “$C$”. From Equation 2:

$$8 G* \left[\frac{3R}{4E*}\right]^{1/3} = C \therefore G* = \frac{C \left[\frac{3R}{4E*}\right]^{-1/3}}{8}$$

With this effective $G*$, the real contact area deduced from Figure 4.8(a) was then combined with the friction data of Figure 4.8(b) to calculate the shear strength in Figure 4.8(c).

This a-C:H:Si:O is an ideal system for performing this measurement. Static friction is high, which allows even a sharp tip to stick to the sample during the stiffness measurement, and low sample roughness (2 Å across 1x1 µm$^2$) limits the dependence of sample friction on local topography. Following this method, the interfacial shear strength $\tau$ was determined for a 25 nm
radius ta-C tip sliding on a-C:H:Si:O in 32±1% RH air, as shown in Figure 4.9. The AFM slow scan was disabled so progressive surface modification occurred from pull-in to pull-off. One

instrumental issue should be noted. Despite turning off the slow scan direction incrementing in the AFM, bending of the AFM cantilever with changing load inevitably leads to a translation of the tip-sample contact position parallel to the cantilever beam.\textsuperscript{31} The total translation of the tip in the slow scan direction was estimated to be 120 nm for the large load range used in this test. This results in less wear at the lowest loads, relative to the highest loads. It also leads to a dependence of the calculated shear strength on the applied load, which can be seen in the non-monotonic variations of the shear strength mirrored in the increasing and decreasing load portions of the trace. This is related to small changes in the local a-C:H:Si:O roughness experienced by the tip, which subtly change the real area of contact, and therefore both the friction and the calculated $\tau$.

The divergence of $\tau$ at the smallest loads (e.g. below 0 nN in Figure 4.9) is typical of these measurements, and is believed to be due to small errors in the calculated contact area

![Graph](image-url)
that lead to large errors in the calculated $\tau$ at small load, due to the real contact area’s position in the denominator of the $\tau$ expression.

In Figure 4.9, $\tau$ decreases up to 28% at a given load during the measurement across much of the load range as indicated by the arrow. This demonstrates that one of the processes occurring during the running-in process is a reduction in the interfacial shear strength. The largest differences occur at intermediate loads between 25 and 70 nN. There are at least two reasons for this. The first is that the surface modification does not change $\tau$ monotonically with load. At the lowest loads while sliding in humid air, the friction could actually increases on the modified surface as was seen previously in Figure 4.6. This is apparent in the crossover in both friction and calculated $\tau$ that occurs around 17 nN load, as seen in Figure 4.9 and its inset. At high load, the reduction in the shear strength difference is likely related to the rapid change in the a-C:H:Si:O with wear. Friction is calculated by measuring the difference between the lateral forces measured during subsequent passes of the probe in opposite directions. If the surface is modified (and the friction reduced) during the first pass of the probe, as is likely at high normal loads, during the second pass the probe will experience lower friction and the calculated friction force will be reduced.

![Figure 4.10: Pulloff force measurements across unworn regions of a-C:H:Si:O in dry or humid N$_2$ using a single crystal diamond probe. Pulloff force measurements were captured across an 8x8 area grid. Average ± standard deviation values are tabulated in the legend.](image)
The measured $\tau$, regardless of surface modification effects, is at least an order of magnitude higher than previous estimates of $\tau$ from DLC sliding experiments at larger lengthscales.\textsuperscript{32–34} To confirm that the result is reasonable, the interfacial shear strength was estimated based on the measured friction during the increasing load portion of the measurement at 25 nN load and assuming simple Hertzian mechanics for the contact. This yielded $\tau = 3.9$ GPa. This is in close agreement with the value determined by measuring the shear stiffness. Additional measurements of $\tau$ were performed with a single-crystal diamond AFM probe and showed qualitatively similar results (Figure 4.8c), though the magnitude of $\tau$ was modestly higher and there was no crossover observed in the friction at low loads.

**Humidity Effects**

To examine the humidity dependence of friction on a-C:H:Si:O, interfacial shear strength measurements were performed in controlled environments of dry (<1% RH) and humid (50±1% RH) nitrogen. At the macroscale, DLCs universally show a substantial difference in friction between humid and dry environments.\textsuperscript{35} A series of AFM tip pull-off force measurements were performed on the as-deposited a-C:H:Si:O in both environments with a ta-C tip which showed there was no statistically significant difference in the adhesion between the two environments (Figure 4.10). This implies that, for this tip-sample geometry, capillary formation does not occur.

![Figure 4.11: Shear strength measurements for a ta-C tip sliding on a-C:H:Si:O in alternating dry and humid N\textsubscript{2} environments. (a) Comparison of results with slow scan enabled to results with slow scan disabled i.e. reciprocating sliding. (b) Comparison of reciprocating sliding in subsequent repetitions of the measurement showing a continuous decrease in shear strength due to a progressive tip change.](image)
on the as-deposited sample. For the shear strength measurements, the radius of the tip was determined with blind tip reconstruction using a UNCD sample before each test, the lateral stiffness was independently measured for each test, and the tests were repeated to ensure trends were robust against tip changes. For each trial, tests were performed with the slow scan direction enabled and disabled to aid in comparison of τ for modified and unmodified regions of the surface. The results of these tests are presented in Figure 4.11.

The measured τ in the two environments were similar. For the surfaces modified by disabling the AFM slow scan incrementing during imaging (Figure 4.11a), τ was substantially lower than on the unmodified surface. The results for the slow scan enabled images display more variability due to sampling a changing topography which modifies the measured friction throughout the scan. A clear determination about which environment led to lower friction on the modified surface could not be made due to a slow change in the tip with progressive wear (Figure 4.11b). This is attributed to a changing surface structure of the tip, rather than the geometry, since this technique should account for the geometry of the tip apex. Additionally, absent tip fracture, an increasing tip radius due to wear is expected to increase friction via growth in the real contact area, whereas in this case a monotonic decrease in friction (as well as τ) was observed over time at constant normal load. It is clear from the results, however, that τ
decreases substantially due to surface modification. These tests were also performed with single-crystal diamond AFM probes, and qualitatively similar results were obtained (Figure 4.12).

![Graph showing shear strength versus normal force](image)

Figure 4.12: Shear strength determined for a single crystal diamond tip sliding on a-C:H:Si:O in <1 or 50±1 %RH N₂. A 2 KHz, ±1.8 nm lateral oscillation used for stiffness measurement. Imaging parameters for “reciprocating” scans: 200 nm scan size, 512 cycles, normal force increment ±0.08 nN. Imaging parameters for “imaging” scans: slow scan on, 1x1 μm² scan size, 128 lines, normal force increment -0.34 nN.
Other Materials

To see if the behavior discussed above could be generalized to other DLCs, similar tests were performed on technologically important hydrogenated amorphous carbon (a-C:H). Results from these tests using a ta-C AFM probe are presented in Figure 4.13a. In this case, repeatability was good enough to delineate a clear hierarchy in $\tau$ with sliding environment. $\tau$ on the modified surface was clearly lower in the humid environment. This result is contrary to expectations based on macroscale experiments, where a-C:H shows substantially lower friction in inert environments.

Figure 4.13: a) Shear Strength as a function of applied normal load for a ta-C AFM tip sliding on a-C:H in dry or humid N$_2$. All measurements performed with slow scan OFF. b) Friction vs. applied load for a ta-C AFM tip sliding on $\mu$-crystalline diamond in two environments. Trials 1 & 2 for each environment were performed immediately sequentially on the same sliding region. The set of trials in each environment were performed sequentially with the same tip but on different areas of the sample.
In addition to the a-C:H, microcrystalline diamond (µc-d) was tested since this material is expected to be lubricated through a similar mechanism to a-C:H and a-C:H:Si:O, with wear-induced dangling carbon bonds passivated by environmental species. This particular µc-d had its surface intentionally hydrogen-terminated after growth. This process prevented the determination of τ since the static friction was too small to oscillate the tip without slipping.

Instead, friction vs. load measurements were made in the dry and humid environments with the slow scan disabled. These are presented in Figure 4.13b. This surface had a high roughness (5.2 nm over 500×500 nm²) which increased the variation of friction across each image. During the first friction vs. load trial in each environment, there were transient excursions to much higher friction (note the log friction scale), with the inert environment leading to much larger and more frequent excursions. The change in normal load during these excursions is attributed to cross-talk between the normal and lateral force channels. Subsequent scans do not show this behavior. We attribute the high-friction transients to the formation of strong adhesive junctions across the counterface, most likely due to bonding with wear-induced carbon dangling bonds, in accordance with the prevailing theory of lubrication in this system. The increased strength of

Figure 4.14: a) Endurance test of reciprocating sliding of ta-C probe on a-C:H:Si:O with an applied load of 20 nN. Inset shows friction response over initial 1000 cycles of sliding. b) Topographic image of sliding region after test in (a) showing blistering of contact region. c) Linescan of blistered region in (b).
these bonds, as indicated by the maximum friction, in the low humidity environment suggests that either water vapor provides protection against wear-induced removal of passivating species or repassivates these dangling bonds before strong adhesive junctions can form. In any case, this behavior is limited to the µc-d system and analogous behavior was never observed in the a-C:H or a-C:H:Si:O systems.

Endurance Testing

While the friction tests above provide insight about the running-in process observed at the macroscale, among other limitations such as much lower sliding speeds, they do not capture a representative sliding history compared to that experienced at macroscale, where running-in requires at least dozens of passes by a sliding contact with µm-scale nominal diameter. To better simulate the effect of this much larger sliding history, longer nanoscale sliding tests were performed (>160,000 vs. <600 sliding cycles in the tests presented earlier). Multiple ta-C probes were subjected to reciprocating sliding on initially unworn a-C:H:Si:O. The scanning pattern was a 50 Hz sine wave of amplitude 225 nm. The friction signal was captured via a lock-in amplifier synchronized with the scanning signal. The output signal was approximately a square wave, so

Figure 4.15: Comparison of friction force traces for a ta-C probe during reciprocating sliding at 100 nm/s across 100 nm on MoS₂ or a-C:H:Si:O either at the start of a reciprocating wear test or after 128 cycles of sliding.
the friction output was corrected by a factor of $\pi/4$ to account for the Fourier content of the square wave.

Figure 4.14a shows a representative friction trace for such a test performed with an applied normal load of 20 nN, corresponding to a maximum DMT contact pressure of 3.2 GPa for this 41 nm radius probe. The inset shows typical behavior for the first several hundred cycles of the sliding test, with a modest friction drop. The remainder of the test shows an additional reduction in the friction, but not of a large enough magnitude to explain the very low shear strengths measured at macroscale. Post-test imaging of the worn region of the film (Figure 4.14b) reveals that the worn region actually grows in height. This is direct evidence of shear stress-induced restructuring of the near-surface layer of the film. It has been shown numerous times in the past that wear tracks of DLC experience some degree of rehybridization of the sp$^3$ carbon to sp$^2$. This rehybridization is accompanied by a reduction in density. Hence the film swells in this region, about 2 nm in this case (Figure 4.14c). This phenomenon may play a minor role in macroscale DLC friction reduction, since this blistering effect will cause regions of high local stress (i.e. asperity summits) to experience the greatest degree of swelling, thereby separating the counterfaces and reducing the real area of contact. It is also possible that this effect is counterproductive for reducing the friction, since this will also result in an increase of local pressure in the highest stress regions, which could result in cleavage of the bonds of passivating species. The constant shear strength of single asperity contacts across a wide range

![Figure 4.16: Schematic illustration of surface passivation effect which is a hypothesized mechanism for the nanoscale run-in effect.](image)
of loads, as shown earlier in this chapter, suggest that such an effect might require extremely large contact pressures to affect the friction to a measurable extent though.

**Detailed Tip Dynamics**

To evaluate what is actually causing the reductions in friction during nanoscale run-in, reciprocating sliding tests were run with ta-C probes on unworn a-C:H:Si:O using high speed data capture to see if the tip dynamics during sliding could reveal any details about the mechanism(s) of friction reduction. Examination of the traces on short timescales revealed that the force dynamics were characterized by aperiodic slips, analogous to the periodic stick-slip phenomenon often seen on crystalline materials like HOPG and MoS$_2$.$^{40}$ This can be seen in Figure 4.15. The stick-slip effect in crystalline materials is attributed to temporary pinning of the probe apex at atomic lattice sites until the constantly increasing lateral force is able to overcome the potential well, often described by the Prandtl-Tomlinson model.$^{41,42}$ We hypothesized that a similar pinning effect was occurring here, either due to covalent bonding across the interface or at topographical wells in the rough a-C:H:Si:O surface. The friction reduction during run-in would be due to surface passivation via replacement of high energy carbon surface reconstructions.

![Figure 4.17: Illustration of analysis method for counting slips during sliding. The traces were generated by smoothing then taking the time derivative of the data presented in Figure 4.15. The selected threshold value for counting a “slip” is shown as a horizontal purple line.](image-url)
with low energy passivating -H or -OH groups, or via polishing of the surface to remove nanoasperities and eliminate the topographical wells causing the probe pinning.

To evaluate the hypothesis, a Ph.D. student in the Carpick group, Zac Milne, performed dynamics modeling using an implementation of the multi-bond model.\textsuperscript{43,44} The multibond model assumes a population of abstract sites on the surface which can represent chemical bonding sites or minima in the energy landscape due to roughness. These sites can form bonds with the sliding tip at a rate controlled by Arrhenius 1\textsuperscript{st} order kinetics:

\[
k_{on} = \omega_{on}^0 e^{\left(\frac{\Delta E_{on}}{k_B T}\right)}
\]
where $\omega_{on}^0$ and $\Delta E_{on}$ are the attempt frequency and the barrier height for bond formation.

There is also a rate of debonding, also controlled by Arrhenius kinetics and modified by a stress assistance term due to the spring force of the cantilever:

$$k_{off}(f_i) = \omega_{off}^0 e^{\frac{\Delta E_{off}(1-f_i/f_c)}{k_B T}}$$

Figure 4.18: a) Friction and slips per cycle during a reciprocating sliding experiment of a ta-C probe on a-C:H:Si:O with an applied load of 30 nN in <5 %RH N$_2$. b) Counted slips per cycle as a function of the friction with a linear fit of the data.
where $\omega_0^{\text{off}}$ and $\Delta E_{\text{off}}$ are the attempt frequency and the barrier potential height in the absence of the external spring force and $f_c$ is the critical force where the barrier vanishes.

Simulations were done which generated the expected force trace as a function of the number of bonding “sites” in the contact area. To be able to compare the simulation results to the experiments, the simulation data was sampled at the same rate as the experiments and the simulations were performed with matching parameters for the sliding speed and spring constant. To quantify the changes occurring during the experiment and simulation, the force traces for both were subjected to identical analyses: Savitsky-Golay smoothing with identical parameters, taking the derivative with respect to sliding distance, then counting the number of slips by setting a threshold value that registered a “slip” every time the derivative trace exceeded this value.

![Figure 4.19: Results of multibond model simulations performed by Zac Milne. Number of slips is plotted as a function of the input number of bonding sites as well as the average friction.](image)

The analysis technique is illustrated in Figure 4.17. Cursory examination reveals that the frequency of counted “slips” changes over the course of the a-C:H:Si:O reciprocating sliding experiment. The analysis technique was then applied to each cycle across the entire experiment. The results are presented in Figure 4.18. Figure 4.18b shows that there is a negative correlation...
between the slips per cycle and the friction. This correlation can be quantified with the Pearson correlation coefficient, which has a value of -0.627. The fact that the friction trace is non-monotonic during the experiment (Figure 4.18a) and that the correlation with slips per cycle holds during the non-monotonic portion of the experiment lends further credence to the idea that the metric of slips per cycle is related to the resulting friction behavior.

To examine whether our hypothesis that the number of “sites” available for bonding changes during run-in and leads to the changes in friction is valid, Zac Milne’s multibond model simulations were run with various numbers of “sites” and analyzed in an identical fashion as the experiments.

![Figure 4.20: Pearson correlation between friction and counted slips as a function of the selected threshold for both experimental as well as simulation results. The dotted line shows the minimum magnitude of correlation often cited as evidence of a significant correlation.](image)

The number of bonding sites is an input parameter into the simulations. The true number of such sites, if they exist, is unknown for the experiments. The results of these simulations are presented in Figure 4.19. It can be seen by the overlapping traces whether the X-coordinate is average friction or the input number of sites, that there is a perfect correlation between the input number of sites and the resulting average friction. As intuition would suggest, an increase in the number of possible sites for bonding directly leads to an increase in the average friction. More relevant to understanding if slip counting provides a useful metric for understanding the
mechanism of friction, there is a correlation between the number of sites and the number of slips which are counted. Over a broad range of friction and numbers of sites, there is qualitative agreement with experiments i.e. decreasing friction with increasing numbers of counted slips. This change is due to a decreasing number of bonding sites in the contact area, as hypothesized. However, for a small number of bonding sites (<20), the number of slips decreases with friction, in contradiction with the experiments.

One criticism that could be made of this approach to studying the friction response is that the choice of threshold used to count slips in the derivative trace is arbitrary. To address this, the Pearson correlation coefficient between the friction and the number of slips was calculated for a range of threshold choices. The correlation in the simulation case was calculated for simulations where the number of sites ranged between 20 and 150. This is shown in Figure 4.20. It is clear that for both the experiments and the simulations, there is a very weak dependence of the degree of correlation on the choice of derivative threshold. Therefore, the particular choice of threshold does not have a large influence on the correlations discussed here. It is interesting that the correlation becomes positive in the case of small threshold values. We attribute this to the fact that the standard deviation of the friction trace increases in both the simulations and the experiments with increasing friction magnitude. Hence, this positive correlation is likely a consequence of this increased variability.

Discussion
The first notable result presented was that the load dependent nanoscale friction on the a-C:H:Si:O is similar to Si but much higher than on HOPG. This is in agreement with previous nanoscale studies demonstrating that nanoscale friction on as-deposited DLCs is comparable or higher than various materials that are not as lubricious at macroscale, including Si, CoPtCr, and muscovite mica. Many different processes can operate in macroscale contacts that do not occur at the nanoscale, and some of these can be used to rationalize these results. For instance, friction for macroscale sliding of various materials against Si is influenced by the formation of hard third bodies which accelerate wear and increase friction. Likewise, for the
layered materials (mica and HOPG), at the macroscale these materials are polycrystalline, exposing their reactive grain boundaries to the counterface where they can modulate the friction, as well as requiring shear between adjacent layers, a process generally not probed in AFM experiments.\textsuperscript{48,49} Nanoscale friction on these layered materials is typically measured across a continuous single crystal where interactions are minimized by the lack of dangling bonds. In this way, one could rationalize the seemingly high nanoscale friction of the a-C:H:Si:O as due not to its poor lubriciousness, but rather due to the fact that the materials it is compared to are much more lubricious on the nanoscale.

Given macroscale results in similar DLC systems suggesting low interfacial shear strengths, the interfacial shear strength measurements presented above require further explanation. While it is true that at the macroscale many additional processes are operative, the measured friction force can still be understood via two parameters: the interfacial shear strength (not necessarily constant throughout the contact) and the real area of contact. Interfacial shear strengths have been estimated for macroscale sliding experiments on DLCs in the past. The few measurements that have been done, including two on a-C:H:Si:Os, arrive at interfacial shear strength values of <100 MPa, and <10 MPa in some cases.\textsuperscript{32–34} These are more than an order of magnitude below the values determined in this study. It is possible these estimates do not accurately determine the real area of contact, but this is a task that the surface force apparatus excels at,\textsuperscript{34} and the Hertzian friction scaling used to assume the form of the contact area in the other studies is persuasive.\textsuperscript{32,33} There is also evidence that the transfer films which typically form in nanoscale sliding experiments are soft and polymeric (in Chapter 3 for instance), which supports the high real area of contact posited by these studies.\textsuperscript{50}
<table>
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<td>Schall et.al.</td>
<td>60</td>
<td>MD</td>
<td>a-C:H/a-C:H</td>
<td>flat/flat</td>
<td>11</td>
<td>24</td>
<td>yes</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.3</td>
<td>0.6</td>
<td>no</td>
</tr>
</tbody>
</table>

Table 4.1: Parameters calculated from published simulation results involving an a-C:H or hydrogen terminated amorphous carbon (h-DLC) sliding against itself, diamond, or hydrogen terminated diamond (h-diamond), where the simulations have been performed with molecular dynamics (MD) or tight-binding quantum chemical molecular dynamics (TB-QCMD).
These prior measurements of $\tau$, if correct, indicate that the nanoscale experiments presented here do not capture all of the processes that lead to their technologically important lubricity at macroscale. These results are also a complication for the dominant theory of lubrication for these materials, which implies that surface passivation of dangling bonds is sufficient to ensure low friction.\textsuperscript{51,52} Many studies have confirmed that surface passivation is operative at macroscale and simulation results\textsuperscript{53-55} indicate it is an effective mechanism for reducing interfacial shear strength, but it is clear that for the a-C:H:Si:O/ta-C system studied here, where environmental or H-dopant surface passivation should occur, that this is not a sufficient condition to ensure lubricity. Additionally, if a lack of surface passivation leads to bonding across the a-C:H:Si:O/ta-C interface, which is the primary consequence of a lack of surface passivation, why is the adhesion on a-C:H:Si:O and HOPG equivalent when there are no such bonds across the HOPG/ta-C interface?

Prior simulation results\textsuperscript{53,55-60} provide context for understanding the high shear strengths measured in this study. In several simulation studies, for diamond or a-C:H sliding against a-C:H counterfaces, sufficient information is provided to allow estimation of the shear strength and normal pressure during the simulations. These estimates are provided in Table 4.1. In studies where the load dependence of friction was examined, it was universally found that the shear strength possessed a strong dependence on the normal pressure. This contradicts the nanotribology results presented here as well as the prior estimates of DLC shear strength discussed above. Nevertheless, some agreement with the experiments presented here could be found in the order of magnitude of the shear strength calculated from simulation results at particular normal pressures, even in cases where the authors affirm that surface passivation is operative during the simulations.\textsuperscript{56,57} Some simulations found much lower shear strengths than those observed in the experiments however.\textsuperscript{55,59,60} In these cases, the authors conclude that a lack of interfacial bonding is critical to achieve these very low friction values. Further comparison between experiments and simulations is hampered by the many differences between the experiments and these simulations: lack of SiO$_x$ in the simulated materials, often much higher normal pressures examined in the simulations (the highest mean contact pressure attained in the experiments was 4.4 GPa), much higher sliding speeds in simulations (20-100 m/s vs. $10^{-7}$ m/s in the experiments), different contact geometries (ultrathin film on infinitely hard
substrate, only one simulated AFM tip geometry, negligible counterface roughness), and the lack of a gaseous ambient environment in the simulations.

Providing further context about the processes occurring at macroscale is the humidity dependence of $\tau$. Sliding the AFM tip on a-C:H:Si:O in dry $N_2$ does not lead to a reduction in friction, as was observed at macroscale for this material (see Chapter 3) and universally for other substantially hydrogen-doped DLCs. In fact, there was no clear dependence on humidity for the a-C:H:Si:O, while for the a-C:H, $\tau$ was actually smaller in the humid environment, a result which contradicts expectations based on macroscale results. One other study indirectly confirming the lack of friction dependence on humidity at nanoscale could be found.\(^5\)

The preceding results do capture one important process relevant to the running-in of a-C:H:Si:O. Repetitive sliding on the surface causes a substantial reduction in $\tau$. DLCs characteristically demonstrate a running-in behavior at the macroscale where the friction coefficient decreases, generally monotonically, before achieving a stable steady state friction coefficient.\(^{32,38}\) The reduction in interfacial shear strength measured here is likely an important contributor to this behavior, along with others such as asperity removal and the formation of a tribofilm. The specific structural changes which occur at the surface of the a-C:H:Si:O to effect this change are unclear based on the AFM friction evolution alone, but prior characterization of macroscale wear tracks and simulation results provide some likely possibilities. It has been shown repeatedly that sliding in environmental gases leads to an enrichment of species such as hydrogen and hydroxyl groups at the surface which can terminate surface dangling bonds in the wear tracks, and thereby reduce friction.\(^{23,38,51}\) Likewise, simulation results show how the wear process in DLCs can cause a restructuring of the surface layers, weakening them and allowing for velocity accommodation.\(^{6,55}\) The latter process is unlikely to play a major role here, given that AFM imaging of the modified regions did not always show discernable wear, even after a substantial reduction in $\tau$ during the surface modification process, but the former process is a reasonable explanation for what is observed. However, the slip dynamics examined using multi-bond modeling indicate a second mechanism is also a reasonable explanation for these changes: surface polishing to remove nanoasperities. The bonding “sites” in those simulations could be
nanoasperities which create tip pinning sites instead of literal interfacial bonds. None of the results presented here allow for discrimination between the two explanations for the dominant friction mechanism in these experiments.

The multi-bond model simulations achieved some modest success in explaining the dynamics observed. The results were, however, ambiguous in that over some range of the numbers of simulated sites, the results contradicted the experiments. The multibond model would need to be used to make further predictions that could be tested experimentally before this approach achieves substantial success in explaining the mechanisms leading to friction reduction during DLC run-in at nanoscale. Nevertheless, the initial results present a promising approach for using AFM friction data to gain insight about mechanisms controlling friction.

One final aspect that should be considered is the lack of quantitative repeatability in the magnitude of friction reduction that characterized the results, which foreclosed the possibility of doing more detailed modeling of the system to learn e.g. if the surface modifications obey an Arrhenius relationship that would allow for determination of an average activation energy for the restructuring of the a-C:H:Si:O which leads to the friction reduction. This suggests that all relevant parameters affecting the process are not controlled in the experiments. An example of this was a slow change in the surface structure of the ta-C probe with increasing sliding cycles that led to continuously decreasing friction. Others might exist which will need to be understood before a more complete picture of the processes occurring in these nanoscale contacts can emerge.

Conclusions

Nanoscale sliding on a-C:H:Si:O shows that with repeated sliding cycles at high normal loads, friction decreases substantially over most loads, except at the very lowest loads. These changes can be measured, post-sliding, over the modified region of the DLC showing that lasting changes to the a-C:H:Si:O surface have occurred. Measurements of the interfacial shear strength show that this parameter decreases across most or all of the tested load range. This process can be used to partially explain “run-in” which was observed at nanoscale on this a-C:H:Si:O and is a
characteristic feature of macroscale sliding on DLCs. The actual measured interfacial shear strength is more than one order of magnitude higher than all previous estimates of interfacial shear strength during macroscale sliding on DLCs, suggesting that there are other processes present in macroscale experiments that do not manifest during this nanoscale sliding. It also indicates that the surface passivation theory of lubrication in DLCs is incomplete since these experiments have the necessary features for low friction according to that theory.

Environmentally-dependent measurements in dry and humid environments show no environmental effect on the measured interfacial shear strengths for the a-C:H:Si:O. For measurements on a-C:H, the interfacial shear strength is repeatably lower in the humid environment. Both of these results contrast with the behavior known from macroscale results. The reason for this lack of dependence could not be determined from AFM results alone, but these experiments provide context for understanding what processes occur at the macroscale which cause the strong environmental dependence observed at that lengthscale. Certainly, the lack of a tribofilm is one major difference between these experiments and the macroscale results. The experiments in the next chapter will provide additional context about the role of the tribofilm on the environmental dependence of friction.

References


132


CHAPTER 5 – Microscale Tribological Response

Introduction

The microscale contact size represents an intermediate lengthscale between the macroscale contacts examined in Chapter 3 and the nanoscale ones in Chapter 4. At first glance, it is not obvious why one should interrogate this lengthscale. The contact geometry is similar to that found at macroscale: composed of at least hundreds of individual asperities, each of which should exhibit a tribological response with similarities to what was found in Chapter 4. This geometry generally forecloses the possibility of using contact mechanics to understand the evolution of important parameters such as real contact area and stress distributions near the interface. However, the possibility of growing a tribofilm is advantageous since there is strong reason to believe, based on the results of Chapters 3 and 4, that the tribofilm is the primary friction reduction mechanism for this system. However, tribofilms were grown and characterized in Chapter 3.

The advantages of working at this scale become apparent when considering the testing implementation. The tests to be discussed were performed with colloidal AFM probes. The use of spherical colloids allows for expansion of the possible counterface chemistries and structures relative to sharp AFM probes, where one is limited to a few materials such as Si, diamond, and DLC. The use of an AFM for testing opens up the possibility of making measurements that are difficult or impossible at macroscale, such as the level of adhesion or the characterization of counterface morphology in-situ. One particularly useful capability is modulation techniques. Of relevance to such studies is the ability to measure the normal stiffness of the contact during the test, which provides insight about the mechanical properties of the sliding contact.

The tribology of DLC has been examined at microscale in the past. Several studies utilize nanoindentation equipment to perform “scratch testing”, where the sharp nanoindentation probe is dragged along the DLC surface with a controlled normal load and, sometimes, resolution of the resulting lateral forces. The wear tracks from such tests can also be characterized in-situ in some cases. These tests are especially good for characterizing the
quality of adhesion between thin films are their substrates. Understanding this adhesion has been critical for the hard drive industry to develop protective overcoats for their magnetic media, and so there has been significant work in this area. The extreme conditions during these tests are also useful for characterizing the wear resistance of the coatings themselves, which again is relevant to the hard drive industry.

Using colloidal AFM probes to study the tribological response of DLC in a similar fashion to what will be discussed in this chapter is rare in the literature. Only two such studies could be found. In one case, colloidal AFM was used to evaluate the effect of micropatterning and ionic liquid lubrication on DLC microtribological response using a polystyrene ball. The lateral forces were uncalibrated so only relative friction performance between the various DLCs could be evaluated. The linear rise of friction with normal load also showed that the contact maintained a multi-asperity contact geometry. In the other study, a very close analog to the experiments which will be presented was run, involving steel colloidal probes sliding on another a-C:H:Si:O. In these tests it was found that the macroscale run-in effect was observed, as well as a similar dependence of friction on humidity as is observed at macroscale. Finally, it was concluded, based on post-test imaging, that the formation of the tribofilm was responsible for the run-in effect.

**Experimental Methodology**

All experiments were conducted in the same RHK 350 AFM housed in an environmentally controlled chamber discussed in Chapter 4. Steel colloids with composition and mechanical properties close to those of the 52100 bearing steel balls used in Chapter 3 with nominal diameter of 40 µm (SHS7574HV1, NanoSteel Company, Inc., Providence, RI, USA) were glued onto tapping mode cantilevers (NCHR, NanoWorld AG, Neuchâtel, Switzerland) using epoxy (JB Weld, JB Weld Company, Atlanta, GA, USA). The colloid apex geometry was characterized by reverse imaging of a calibration sample (TGT1, NT-MDT Spectrum Instruments, Moscow, Russia) composed of Si spikes with apex radii below 30 nm. Normal forces were calibrated using the pure thermal tune method. Lateral forces were calibrated using the diamagnetic lateral force calibration. Sliding tests were performed on the same a-C:H:Si:O discussed in chapters 2-4 (from NCD Technologies, Inc.) in either dry nitrogen (<5% RH) or humid
nitrogen (50±5%RH), controlled by continuous flow of nitrogen from the boiloff of a liquid nitrogen dewar, with some fraction bubbled through deionized water to provide humidity when needed.

During high-load, reciprocating sliding tests a vertical sinusoidal oscillation of 50 pm amplitude at 3 kHz was applied to the Z-piezo. The frequency was chosen to be above the low-pass filter cutoff of 2 kHz for the feedback circuitry so the normal force feedback was unaffected. The normal force signal was fed into a lock-in amplifier using the Z-oscillation signal as a reference, so that the lock-in output provided the force response to the oscillation signal. This technique is referred to as force modulation microscopy (FMM).14

**Results**

One of the goals of this study was to grow a tribofilm in-situ after failing to grow one in the single asperity experiments of Chapter 4. To achieve this, a bare steel colloid of apex radius 50 µm was subjected to reciprocating sliding at a deliberately high applied normal load of 1 µN across a scan length of 2 µm. With an adhesion force of 256 nN determined via the pull-off force measurement, a Derjaguin-Müller-Toporov (DMT)15 estimate of the maximum normal contact pressure and contact radius were 85 MPa and 78 nm, respectively. It should be noted that since this is a multi-asperity contact, as will be shown later, there are asperities which will experience
higher normal stresses and the real area of contact will be much smaller than the DMT contact radius would imply.

Figure 5.1: Various signal channels during reciprocating sliding at 4 µm/s across a 2 µm wear track of a steel colloid on a-C:H:Si:O with a 1 µN normal load. A 50 pm, 3 kHz Z-oscillation was applied during the test, which allowed for tracking of the normal stiffness and phase.
Figure 5.1 shows the evolution of various parameters during the reciprocating sliding test. At the start of the test through approximately cycle 200, the friction increases substantially. The contact stiffness increases modestly, and the degree of phase lag between the normal oscillation and response also increases. There is no observable change in the topographic height. Two plausible explanations for the friction increase are that asperities are being removed from both counterfaces thus increasing the true contact area, and/or the oxide layer is being removed from the steel, thus exposing the more adhesive and reactive bare steel, which exhibits a higher shear strength. The former would lead to an increase in the real contact area, which increases the normal stiffness and friction. The latter would increase friction due to increased shear strength. In addition, more adhesion and greater contact area would increase formation of adhesive junctions with the exposed bare steel.
Starting at cycle 210, the friction begins to drop precipitously at the same time the normal stiffness and phase lag jump, and the topographic height begins to increase. This is clear evidence of the nucleation and growth of a tribofilm. This process occurs over approximately 120 cycles. The topography signal change is due to the probe being lifted by the feedback circuit to maintain a constant normal load, consistent with the growth of a tribofilm on the probe. The increase in the normal stiffness indicates that the real contact area grows substantially, if the assumption is made that the tribofilm possesses similar mechanical properties as those grown at macroscale and characterized in Chapter 3. It was found in that case that the tribofilms had much lower average elastic moduli than the initial counterfaces, and such a change in mechanical properties should directly reduce the normal stiffness. That the friction is primarily controlled by the tribofilm formation is also confirmed by the friction image in Figure 5.2, which is constant across the wear track (except at the edges where the effect of static friction produces an artificial apparent low friction force). If friction were controlled by changes to the a-C:H:Si:O, one would expect a friction dependence on position in the wear track (i.e. vertical features in Figure 5.2).

For the remainder of the test, the changes are less dramatic. The topography continues to grow before saturating at a tribofilm thickness of 28.4±2.3 nm. Notably, the friction is approximately constant during this growth, indicating that the friction reduction is primarily controlled by the chemistry and structure of the tribofilm near the a-C:H:Si:O/tribofilm interface. Post-sliding imaging did not reveal any transfer of tribofilm back to the a-C:H:Si:O, nor was such reverse transfer ever observed at macroscale. There is a slow increase in the friction and normal stiffness throughout the remainder of the test. These results can be explained by some additional growth in the real contact area as the tribofilm grows in lateral extent due to deformation and wear of the tribofilm. The phase lag also continues to increase during this time, which is an indication of increasing viscoelasticity in the tribofilm, in agreement with what was found for the tribofilms in Chapter 3.
Figure 5.3 shows pre- and post-test reverse imaging of the colloidal probe using a TGT1 sample. The post-test measurement was done in tapping mode rather than contact mode to minimize wear of the tribofilm. It is clear from the linescan that the thickness of the tribofilm (33.6±8.8 nm) agrees reasonably well with the 28.4±2.3 nm which was measured during the sliding test, with the difference perhaps reflecting compression of the tribofilm due to the normal load during the wear test. The tribofilm is elongated in the sliding direction, which agrees with what is typically seen in macroscale sliding. The fact that that the tribofilm forms at an apparent offset from the colloid apex may be due to an experimental issue. The topography was measured by scanning the colloid over a spiked TGT1 sample. A difference in the slope of
TGT1 sample relative to the a-C:H:Si:O sample under the probe of as little as 1° could produce the offset seen here.

Nevertheless, the wide lateral extent of the tribofilm relative to the nominal contact area requires explanation. In Chapter 3, where a similar effect was seen for sliding in a blowing N₂ environment, we attributed this effect to a combination of plastic deformation and viscoelastic flow due to the soft polymeric properties of the tribofilm. Flow out of the contact area may help explain the self-termination of the vertical growth of the tribofilm, with extra tribofilm volume beyond the thickness where the tribofilm is stable being shed out of the contact area and increasing the lateral extent of the tribofilm.

An additional possibility, given that the thickness of these tribofilms are a significant fraction of the nominal contact radius, is that the nominal contact area increases because of a decrease in the reduced Young’s Modulus of the contact due to the formation of the soft tribofilm. In Chapter 3 it was found that all regions of tribofilms grown in a humid environment had elastic moduli <40 GPa, at least a 60% reduction relative to the bearing steel on which they were grown, with many areas exhibiting much smaller elastic moduli. Since the nominal contact diameter in DMT contact mechanics scales with $E^{*^{-1/3}}$, a e.g. 50% reduction in $E^*$ leads to a 50% increase in the nominal contact area, so a substantially reduced $E^*$ due to growth of the tribofilm can produce an equally substantial increase in the nominal area of contact.
To examine the tribological response of the colloid on the a-C:H:Si:O, with and without the tribofilm, a series of friction vs. load measurements were done. The measurements were performed at 3 µm/s across a 5x5 µm² region with a constant normal load change after each of 128 scan lines. The large spatial increment between scan lines (40 nm) was chosen to minimize wear of the a-C:H:Si:O and therefore dependence of the friction on wear-induced changes to the a-C:H:Si:O as well as to minimize any additional growth of the tribofilm. Each image was immediately repeated with a decreasing load to verify repeatability and to capture the load range between pull-in and pull-off. In the bare colloid tests, humid and dry environment tests were conducted. For the colloid with tribofilm tests, a smaller load range was used to minimize damage to the tribofilm. Tests were performed in multiple environments, but it was apparent that the tribofilm was evolving throughout these tests, so only the first is presented since this test had the most similar tribofilm geometry and structure as when it was grown. This was performed in the same humid environment in which it was also grown. All tests were performed on previously unworn regions of the a-C:H:Si:O. Note that the maximum load reached, 470 nN is
significantly less than the 1 µN load used previously to generate a tribofilm on a bare colloid probe.

Results are presented in Figure 5.4. Focusing on the bare colloid results, it is clear that there is a strong humidity dependence to the friction. The linear dependence of friction on load is consistent with a multi-asperity contact geometry.\textsuperscript{17} The ratio of humid to dry friction coefficients is 2 for trial 1, which is in reasonable agreement with macroscale results where this ratio was ~3. Upon continued sliding in the 2\textsuperscript{nd} trial, the environmental dependence becomes less pronounced, with a friction coefficient ratio of 1.4. The only known change to the contact between the trials was an increase in real contact area due to asperity wear. These results are of lesser importance to understanding the macroscale a-C:H:Si:O lubricity, because the relevant comparisons between the macroscale and the microscale are when a tribofilm is present. Nevertheless, the macroscale tests in Chapter 3 showed a humidity dependence from the start of sliding and the bare colloid results confirm this.

The comparison to friction vs. load with a tribofilm present shows some important features. The first is that the adhesion is reduced substantially, by at least 80%. This is remarkable considering the increase in real contact area, to be discussed below. This shifting of the friction vs. load curve to the right results in reduced friction across the entire load range, relative to the bare colloid results. A change from a patchy, multi-asperity contact to a more continuous area of contact is supported by a power law fit to the contact area vs. load (Figure 5.4), where the scaling exponent was 0.52. In the case of assuming a constant shear strength,\textsuperscript{18} the expected scaling exponent for a perfect, single-asperity DMT contact is 0.67, as opposed to the case of a multi-asperity contact which obeys Amonton’s law, where the expected scaling exponent would be 1 (as was seen for the bare colloid). This very low scaling exponent indicates the contact is behaving as a single asperity contact. The fact that the exponent is lower than the lower bound of the range between single and multi-asperity contacts is not fully understood, but may have to do with the fact that the tribofilm is not spherical in shape, but rather more like a flat plateau. It is reasonable to hypothesize that this causes the contact area to grow more slowly with normal load than would be the case for a spherical contact. This can be rationalized by considering the extreme case of a rigid, flat punch. Friction vs. load curves in such a case
It was mentioned before that friction vs. load trials were run in multiple environments for the tribofilm on colloid geometry. These are presented in Figure 5.5 for completeness. It is apparent that there is limited repeatability between the two trials. This may be due to continuous wear of the soft tribofilm. There is no indication of the humidity dependence of the friction that was observed at macroscale. Also, there is no increase in adhesion for the humid environment, showing that capillary condensation does not occur here.

**Discussion**

The compilation of results presented here provide important insight about the basic lubrication mechanisms of a-C:H:Si:O. The reciprocating sliding testing presented in Figure 5.1 represents the clearest evidence in the literature that the presence of a tribofilm is the primary factor leading to low friction in a DLC material. By monitoring multiple parameters, it was possible to detect the growth of the tribofilm, primarily via changes in the stiffness and tip height, and correlate its nucleation to the moment the drop in friction occurs. The closest prior
results have come to accomplishing this is studies that have used a camera peering through a transparent counterface to detect when a tribofilm was present in macroscale sliding experiments either visually or with Raman spectroscopy, but it has been recognized frequently in the past that the formation of a tribofilm is correlated with large reductions in overall friction.

The technique presented here offers additional insights. The termination of the friction reduction after the tribofilm has grown <5 nm in thickness indicates that there is little dependence of the friction on the thickness of the tribofilm beyond a small threshold thickness. This indicates that it is important for researchers to use surface-sensitive spectroscopy to confirm or deny the presence of a tribofilm before making conclusions about what is driving friction reduction in DLC tribology experiments.

One can use these data to gain insight about what is occurring during the friction drop. From the topography trace, the friction reduction occurs progressively as the tribofilm grows 5 nm in thickness. One can use DMT contact mechanics to estimate when contact between the steel and the a-C:H:Si:O is completely lost during growth of the tribofilm. Based on the applied normal load, mechanical properties of the colloid and a-C:H:Si:O, radius of the colloid, and pre-sliding adhesion value, one can calculate the normal deformation of the steel colloid due to the applied normal load. This deflection is <0.2 nm during the experiment. While asperities may deflect more than this due to higher local pressure, the overall roughness of the colloid near the apex is <0.5 nm, so lifting the steel ball 1-2 nm should be more than sufficient to eliminate all direct contact between the steel and the a-C:H:Si:O. Therefore, the friction continues to drop after the steel colloid has lost all direct contact with the a-C:H:Si:O. This suggests that there is some dependence of the shear strength on the tribofilm thickness across a small range of thickness values, apparently up to 5 nm is thickness.

The results present multiple pieces of evidence indicating that there is a very large increase in the real area of contact as the tribofilm grows. The increase in stiffness despite the growth of a very low modulus tribofilm demonstrates an increase in contact area. Unfortunately, despite having a good understanding of the average modulus of the tribofilm from Chapter 3, we cannot quantify the change in real contact area because the tribofilm is thin.
and deposited on top of the much harder steel substrate. The comparison between the friction vs. load curves with and without tribofilm also clearly demonstrates that the real area of contact is much larger in the tribofilm case.

Since we know the real area of contact is much larger in the tribofilm case, we can also conclude, based on the disparity in friction at a given load between the bare colloid and the colloid + tribofilm, that the formation of the tribofilm is accompanied by a large drop in the interfacial shear strength. As the load grows, the difference in friction also grows between the tribofilm and bare colloid cases, as can be seen from Figure 5.4. At some point, upon increasing the load further, in the bare colloid case, the colloid will compress all asperities such that the real contact area is nearly equal to the nominal contact area, and the bare colloid friction will change from linear scaling with load to power law scaling consistent with DMT contact mechanics. This critical load can be estimated from the mechanical properties of the counterfaces and a roughness parameter of the ball, which we know from AFM imaging of the colloid surface. The critical load is calculated to be 20 µN. At this critical load, the real areas of contact for the bare colloid and the colloid + tribofilm should be nearly equal, aside from the growth of the tribofilm beyond the initial nominal contact area. This allows for an estimate of the minimum reduction in interfacial shear strength upon growth of the tribofilm. This will be an underestimate because we know from post-sliding imaging (Figure 5.3b) that the tribofilm grows laterally beyond the initial nominal contact area. Extrapolating the curves displayed in Figure 5.4 for the bare colloid <5 %RH Trial 1 and the colloid+tribofilm to this critical load, one finds that there is an 80% difference in the friction, and therefore at least an 80% reduction in the shear strength. Given the scale of lateral tribofilm growth beyond the initial nominal contact area, the real reduction in the shear strength is likely much larger. It should be emphasized that this reduction in shear strength is much larger than what was found for the nanoscale run-in effect for hard asperity contacts discussed in Chapter 4.

The humidity dependent friction vs. load measurements for the colloid+tribofilm showed that there was no detectable dependence on the humidity. This was unexpected, given a universally strong dependence in macroscale sliding experiments, including those in Chapter 3. One possible explanation is that these experiments do not present a sufficiently accurate analog
to macroscale experiments, where the humidity dependence has been shown on worn films, whereas these friction vs. load measurements were done on unworn a-C:H:Si:O.

Conclusions

In this study, it has been shown, via sliding experiments of a steel colloid on a-C:H:Si:O using an AFM, that a tribofilm can be grown at the microscale with in situ detection of its growth and a simultaneous drop in the friction. The drop in the friction is attributed to two primary effects. The first is an 80% reduction in adhesion, which reduces the friction at any given applied load. The second is a reduction in the interfacial shear strength. The experimental data is detailed enough that a lower bound estimate of the fractional reduction in interfacial shear strength can be made, which shows that the shear strength is reduced by at least 80%. The formation of the tribofilm is accompanied by a large increase in the real area of contact, which would lead to an increase in friction if adhesion and shear strength were held constant. Instead, the reductions in adhesion and shear strength lead to an overall reduction in friction, with the degree of friction reduction increasing at higher applied loads.

References


In this thesis, a number of insights have been gained about the tribological response of a-C:H:Si:O. It was shown at the macroscale that the tribofilm which grows on the sliding counterface is soft and viscoelastic with no evidence of graphite formation within the bulk of the tribofilm. This strongly indicates that the tribofilms have a polymeric structure. Additionally, the tribofilm possesses inherent lubricity as shown by sliding it against a Si wafer and achieving a similar friction coefficient to that found when sliding against the a-C:H:Si:O. The lubricity of the tribofilm was also shown to be substantially independent of its specific composition, given that equally low friction coefficients could be obtained for a Si-rich tribofilm grown during sliding in dry air as for a carbon-rich tribofilm grown during sliding in humid air. Nanoscale sliding of hard diamond or ta-C single asperity AFM probes against a-C:H:Si:O showed that a qualitatively similar friction reduction to that seen at macroscale could be reproduced during reciprocating sliding, which was due to a reduction in the interfacial shear strength. After this run-in process was complete, the shear strength remained approximately constant across a wide load range. The absolute value of the shear strength, however, indicated that the lubricity achieved at nanoscale was at least an order of magnitude worse than what is found at macroscale, based on the metric of shear strength. Agreement between molecular dynamics simulations within the framework of the multi-bond model and the nanoscale experiments showed that the high friction seen at the nanoscale was a consequence of tip pinning at discrete sites on the a-C:H:Si:O. Unfortunately, the multi-bond model simulations run to date cannot distinguish between asperity pinning due to nanoscale roughness or interfacial bonding, which has been posited to be the primary source of friction in DLC systems in the past. Microscale reciprocating sliding experiments between a steel colloid and a-C:H:Si:O showed, \textit{in situ}, that the moment the tribofilm begins to grow, there is a large drop in the friction which plateaued when the tribofilm reached a thickness of \(\sim 5\) nm. A comparison of friction vs. load plots for the colloid sliding on a-C:H:Si:O before and after growth of the tribofilm showed that growth of the tribofilm is accompanied by a large drop in the adhesion, a large increase in the real contact area, and a large reduction in the interfacial shear strength. The drop in interfacial shear strength and adhesion overwhelms the effect of increasing the real contact area to produce an overall reduction in friction.

Comparing the results at the nanoscale to the results at the microscale, some additional context about the friction mechanisms can be gained. As previously discussed, the primary explanation of lubrication for DLC systems is that passivation of the DLC surface with hydrogen or other unreactive functional groups prevent the formation of interfacial covalent bonds which are
the primary contribution to friction in DLC sliding. The formation of a tribofilm is known to be important, but only as an empirical fact; there is no clear physical understanding of how it leads to low friction. We have already established in Chapter 4 that the lubricity of the a-C:H:Si:O against hard, nanoscale asperities is poor, at least in the cases of ta-C and diamond asperities, and at microscale there is a large decrease in the shear strength upon growth of a tribofilm. This would imply that if surface passivation is a sufficient condition for lubrication in a-C:H:Si:O, then passivation of the tribofilm surface is responsible for the shear strength reduction of the interface upon tribofilm growth. It also implies that surface passivation was poor at nanoscale, leading to the high measured shear strengths. The multi-bond modeling of the nanoscale experiments qualitatively reproduces the aperiodic slip that was observed in the lateral force traces during the experiments, and while the bonding “sites” in the model are abstract, “sites” which are covalent interfacial bonds due to the absence of passivating species are consistent with the surface passivation mechanism of DLC lubrication.

Chapter 5 showed that the formation of the microscale tribofilm was accompanied by a substantial increase in the real contact area, and that the average contact pressure decreased as a result, given that the load remains constant. This is potentially relevant to the lubricity afforded by the tribofilm. Simulation results suggest high contact pressures are required to generate the dangling surface bonds necessary for adhesive junctions to form between DLC and the counterface, with a threshold for interfacial bonding of at least 1 GPa (see Table 4.1 in Chapter 4) in the case of self-mated DLC contacts. In the nanoscale single-asperity experiments where lubricity was poor, there was a lower limit on the accessible contact pressures, because elastic energy stored in the cantilever would cause tip pull off prior to reaching zero contact pressure. For the sharp AFM probes used in Chapter 4, the minimum achievable pressure was around 250 MPa. Therefore, a reasonable explanation for the reduction of friction upon growth of the tribofilm (at macroscale or microscale) is that the tribofilm growth reduced the contact pressure below the threshold for formation of interfacial chemical bonds. Upon growth of a tribofilm, the chemistry of the counterface also changes to one which is similar to the a-C:H:Si:O, but better passivated than the steel or ta-C counterfaces used in this work, as suggested by the elevated hydrogen fraction found in the macroscale tribofilms investigated in Chapter 3 and in other studies of tribofilm structure.¹ The better passivation of the counterface likely increases the threshold load to formation of interfacial bonds. This is supported by simulation work showing that hydrogen terminated diamond sliding against DLC had a much higher threshold pressure for interfacial bonding²,³ than self-mated a-C:H.⁴,⁵ That hydrogen terminated diamond is better passivated than hydrogen terminated a-C:H is demonstrated by their relative stability under annealing, where a
temperature of 750ºC is required to break C-H bonds in diamond\(^6\) whereas hydrogen begins desorbing from a-C:H below 400ºC.\(^7\)

Future work on the lubricity of a-C:H:Si:O should focus on the effect of the tribofilm. While the explanation of the tribofilm lubricity as being due to improved surface passivation provided by the reduced contact pressures accompanying growth of the tribofilm presents a plausible explanation for the lubricity afforded by the tribofilm, there is reason to believe there could be additional effects that play a role beyond surface passivation. In a simulation study of self-mated a-C:H sliding, increasing the load led to a rapid increase in shear strength due to increased formation of interfacial bonds,\(^4\) and the other studies in Table 4.1 also showed a strong dependence of the shear strength on contact pressure. This disagrees with the nanoscale results presented here where there was no decreasing trend in the measured shear strength with decreasing load. This is illustrated in Figure 6.1 for the shear strength post-run in (i.e. after the

![Figure 6.1: Normal stress vs. shear strength for a ta-C probe of radius 45 nm during reciprocating sliding on a-C:H:Si:O in multiple environments.](Image1)

friction has stabilized under repetitive sliding), where the shear strength for a ta-C probe remains relatively constant in the GPa range across a normal stress range extending to <1 GPa. Additionally, the shear strengths measured in many of the simulation results of Table 1 in Chapter 4 were also above the range of macroscale estimates of the shear strength for DLC sliding contacts (10-100 MPa), so they may not capture the mechanisms that allow for extremely low shear strengths in the presence of tribofilm.

Simulations are likely the best way to examine the physical mechanisms that lead to extremely low shear strengths for DLC sliding against a soft and viscoelastic tribofilm, given that attempts to grow a tribofilm on nanoscale single asperity contacts for study were generally
unsuccessful. The primary difficulty in performing simulation studies is that the structure of the tribofilm is not known in enough detail to accurately model. One possible solution that would examine the effect of the reduced modulus of the tribofilm would be to construct a standard DLC surface via deposition or liquid quenching, and then reduce the strength of the interatomic potentials in an ad hoc fashion. This would have the effect of reproducing the stiffness reduction of the tribofilm relative to the DLC, though no viscoelasticity would be present. Another approach would be to model the tribofilm as a known polymer with a high density of C-H bonding, such as polyethylene. Such a structure would reproduce both the stiffness reduction and the viscoelasticity of the tribofilm. In either case, we hypothesize that investigators would find that the effect of physical pinning of nanoasperities would be reduced due to the lower stiffness of tribofilm nanoasperities, thereby leading to reductions in the shear strength. The literature offers evidence that the dependence of shear strength on contact pressure is much smaller in the case of friction dominated by asperity or atomic pinning\textsuperscript{8–10} rather than interfacial bonding,\textsuperscript{2,4,11} which would be more consistent with and also explain the constant shear strength as a function of load found in our nanoscale work.

Another aspect of a-C:H:Si:O tribological response that warrants further examination is the humidity dependence of friction. While the effects of humidity are strong at macroscale, such effects were essentially absent in nanoscale and microscale experiments performed here. To address this, we suggest that colloidal probe AFM experiments could be performed as a function of the colloid diameter. Increasing the colloidal probe size must eventually lead to reproduction of the macroscale dependence of friction on humidity. The only experiments in this thesis that reproduced the macroscale friction dependence on humidity seen in Chapter 3 were for bare steel colloids sliding on a-C:H:Si:O, as discussed in Chapter 5. This suggests that a multi-asperity contact might be necessary before a humidity dependence is evident.

a-C:H:Si:O thin films have attractive properties for applications in a number of challenging environments. The rational design of further improvements that will enhance the tribological behavior requires a detailed understanding of its mechanisms of lubrication, a challenge shared with other DLCs. This thesis provides a number of insights about the basic lubrication of a-C:H:Si:O across several lengthscales that can help guide further efforts to achieve this reasonably complete understanding.
References


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APPENDIX – Scanning probe method for accurate measurement and mapping of atomic lattice constants via atomic stick slip demonstrated with measurement of thermal lattice strain in CVD MoS$_2$

Introduction

The family of scanning probe microscopies (SPM), encompassing many modes of atomic force microscopy (AFM) as well as scanning tunneling microscopy, are an important set of tools in laboratories all over the world. As an area of scanning probe research, imaging of surface crystal lattices with atomic resolution has achieved broad success, shedding light on details of the surface reconstruction of free surfaces which are relevant to catalysis and thin film growth and properties. The study of local atomic defects is relevant for understanding how surface defects affect material properties, especially in thin film systems. At the extreme end of such systems are the 2D materials like MoS$_2$ and graphene which have experienced explosive research interest in recent years and are ideal systems for scanning probe study.

Despite their enormous success in advancing all manner of scientific inquiry, scanning probe methods have some inherent limitations. A significant one is lateral resolution, which stems from multiple causes. Lateral interactions with protrusions on the sample cause a convolution of the sample image with that of the AFM probe tip which degrades the lateral resolution of small sample features. Another source is from the tip or sample scanning hardware. Most typically, the raster motion required is achieved with ceramic piezoelectric elements, often composed of a sintered lead zirconate (PZT) powder, which can be formulated to achieve a large piezoelectric coefficient, allowing for large piezo motion with practical bias voltages. The precision of such manipulators can be high, especially for small scan sizes, enabling the acquisition of atomically resolved images across tens of nanometers or larger. Nevertheless, several inherent characteristics of these piezo ceramics limits lateral resolution. Such effects include increasing non-linearity of response with increasing scan size and frequency due to piezo hysteresis, and piezo creep. Some commercial systems correct for these issues by implementing lateral
position sensors which can correct the piezo position to below a few nm but can also degrade atomically resolved imaging due to additional noise caused by the necessary feedback systems.\textsuperscript{12}

The variation in bond lengths and the lattice constant due to e.g. temperature changes or lattice mismatch with a bulk substrate has remained inaccessible by SPM due to the limited lateral resolution. Such information can be determined at a local level if the sample is amenable to the preparation required for tunneling electron microscopy, or at a global level if the sample bulk is large enough to be probed using X-ray diffraction.\textsuperscript{13} Indirect techniques have also been developed, e.g. the Raman measurement of the lattice constants of MoS\textsubscript{2} and graphene where benchmarking indicates substantial success, though lateral resolution remains limited to the \textmu m-scale.\textsuperscript{14-16} Such information can be indispensable since lattice strain can have a significant effect on global properties. The ability to measure local strains could prove useful, given that, e.g. in the case of graphene, nanostructuring can be combined with lattice strain to achieve useful modulation of electronic and optical properties.\textsuperscript{17-19}

This study demonstrates a straightforward technique, which we will call linescan lattice measurement (LLM), using an unmodified commercial AFM to measure the lattice constant and orientation for materials which exhibit the stick-slip instability for the atomic surface corrugation in contact-mode AFM imaging. LLM is used to provide a very accurate scanner piezo calibration scheme valid across large length scales. The degree of absolute accuracy achieved is demonstrated by directly measuring the lattice constant of natural and CVD-grown monolayer MoS\textsubscript{2} and demonstrating that lattice strains in the CVD MoS\textsubscript{2} as small as 0.5\% can be reliably measured.

**Experimental Methods**

All experiments discussed were performed in an RHK350 atomic force microscope with an R9 controller (RHK Tech., Troy, MI). The AFM was mounted in a vibration isolated environmental control chamber. Flowing \textsuperscript{12}N\textsubscript{2} from the boiloff of a liquid nitrogen dewar was used to maintain <5\%RH throughout the measurements. The AFM was operated in contact mode using diamond-coated AFM probes (AD-I-0.5-AS, Adama Innovations, Dublin, Ireland; ND-CTI series, Advanced
Diamond Technologies, Romeoville, IL, USA) for maximum wear resistance, though the technique discussed should be amenable to other probe materials. Sample materials discussed include natural MoS$_2$ and NaCl single crystal (Structure Probe Inc., West Chester, PA), and CVD-grown MoS$_2$ on a SiO$_2$ substrate. In the lattice constant mapping measurements, standard 2D images were acquired. All other measurements were performed via reciprocating scanning at various sizes and frequencies at low loads (<5nN) while simultaneously capturing the normal and lateral force traces at sampling rates high enough that atomic scale periodicities could be extracted from Fourier transforms of this data (i.e. atomic-scale spatial frequencies were below the Nyqvist frequency of the sampling rate.)

**Results**

Figure A.1b shows a Fast Fourier transform (FFT) of a single contact-mode linescan across MoS$_2$ which illustrates the features enabling LLM. Three peaks are apparent in the spectrum (along with their expected reflections at negative spatial frequencies), which correspond to the X-components of the three peaks in the associated image FFT (Figure A.1a). It is a common feature in image FFTs of atomic lattice-resolved contact-mode images that intensity from diffraction spots extends along the slow scan axis (i.e. the Y-axis in Figure A.1a), and it is this intensity which results in the peaks along the X-axis linescan (Figure A.1b) regardless of which X position is used. A mechanism involving slips from individual atomic positions can be used to explain these features.$^{20,21}$ The authors demonstrated that while scanning perpendicular to the cantilever axis, the tip apex can be pinned at atomic positions along multiple atomic rows in the cantilever axis position. What was not appreciated about this phenomenon previously is that the slip behavior, while stochastic at the level of individual slips, on a time-averaged basis, provides periodicity information about all close-packed atomic planes perpendicular to the surface plane. Additionally, FFTs from atomically resolved images which contain diffraction spots
extending along the slow scan direction can also be found in the STM literature where this slip mechanism is absent.\textsuperscript{22–25} We attribute this to the non-negligible size of individual atoms in the lattice, which allows the probe tip to sample the periodicity of all of the close-packed lattice directions regardless of the position and direction of

![Figure A.1: (a) Image FFT of the lateral force channel of a 2D lattice-resolved contact-mode AFM image of bulk MoS\textsubscript{2} and (b) a single linescan spanning the X* axis of the same image. The linescan shows that intensity associated with all diffraction spots is present.](image)

157
a particular linescan. The presence of these features in some STM work suggests the following analysis could be amenable to other scanning probe techniques.

The ability to simultaneously measure the surface periodicity of all three close-packed planes on MoS₂ provides a means to measure the lattice constant and index the surface lattice of the sample with only an individual linescan. If it is assumed that the surface lattice is six-fold symmetric, the reciprocal lattice constant can be calculated as:

\[ a^* = \frac{2\sqrt{X_1^* X_2^* + X_2^* X_2^*}}{\sqrt{3}} \]

where \( X_1^* \) and \( X_2^* \) are the two lowest frequency peak spatial periodicities. Figure A.2 illustrates the relevant parameters and geometry. Similar simple relations can be obtained for the other possible peak pairs. If the lattice parameter is known, the reciprocal lattice orientation can be obtained from:

\[ \theta_i = \cos^{-1} \frac{X_1^*}{a^*} \]
For six-fold symmetric axes an ambiguity remains due to a mirror axis in the linescan direction. This can be resolved by inspection of the real-space normal force channel of the same linescan. As demonstrated by Morita et al., the tip tends to slip along the close-packed plane of atoms oriented closest to the linescan direction, thereby sequentially increasing the magnitude of the buckling force on the cantilever. When the tip slips between these close packed rows, there is a reduction in the buckling force. With knowledge of the AFM coordinate system and the approximate frequency with which these slips occur, the direction of the change in normal force during slip unambiguously resolves whether the associated diffraction spot lies above or below

Figure A.2: Schematic representation of the measured quantities $X_1^*$, $X_2^*$, $X_3^*$ in 2D reciprocal space for a hexagonal lattice such as graphite or MoS$_2$. A mirror symmetry exists for the measurement across the scan direction axis.
the mirror axis. This can be seen in Figure A.3. The low frequency slips apparent in the normal force trace always occur in the same direction.

These slips reduce the buckling force on the cantilever, as illustrated in Figure A.3b. With knowledge of the AFM system geometry, the slip direction in the normal force trace determines whether the reciprocal lattice vector lies above or below the mirror axis, thereby removing the lattice orientation ambiguity. The orientation determined in this fashion will be more accurate than one obtained from 2D imaging due to the lack of piezo creep along the slow scan direction and can be obtained with less tip wear since a small number of linescans are the only requirement.

Figure A.3: a) Example force traces while sliding an AFM probe on natural MoS$_2$ b) Schematic representation of the normal force slips on the atomic lattice measured in (a).
Now we move on to a method in which individual linescans were not analyzed, but rather time-resolved FFTs captured by the AFM software from the normal and lateral force channels. These were obtained from continuously scanning a single line with triangle-wave excitation of the scanner piezos to improve the signal to noise ratio and simplify the measurement. Because each analyzed force trace taken in this fashion spans multiple linescans, there is a phase shift in the stick-slip signal every time the probe tip reverses direction. These phase shifts cause the broad FFT peak near a single stick-slip frequency to be broken up into a comb structure. This is demonstrated in Figure A.4 for the case of spatially-resolved data. The spacing of the spikes in the comb structure is equal to the inverse of the linescan length (or linescan duration for temporally-resolved data). This spacing of the spikes in the comb structure is also equal to the spacing of the datapoints in the FFT of an individual linescan, so the useful frequency resolution remains unchanged. In both cases, longer linescan lengths correspond to higher useful frequency resolution of the stick-slip periodicity, but also broadening of the peak or comb structure due to increasing piezo hysteresis.

![Image](image.png)

**Figure A.4**: Comparison of FFTs from 50x50 nm², 1024x1024 pixel² image computed in 2 different ways: averaging FFTs from the 1024 individual scanlines or combining all data into a single 1D line prior to FFT. The data brackets a single atomic stick-slip peak.

**Scan Piezo Lateral Calibration**

The measurement discussed above forms the basis for a new scanner piezo calibration technique that can, in principle, be valid across any lengthscale. Drift has minimal effect on the
result since scanning speeds can be chosen which are very high relative to any plausible drift rate, thereby rendering the drift error negligible.

By measuring the lattice constant in this fashion on a reference sample (natural MoS$_2$ in the following), correct piezo calibration constants can be determined for the lengthscale of interest. For the data presented here, data was captured at 97.6 KHz, for 5.369 s and an FFT performed. Twenty sequential FFTs were averaged to generate the spectrum for analysis and the stick-slip frequencies chosen were those of maximum intensity. A calibration curve for the RHK350 is presented in Figure A.5 as a function of the maximum voltage of the triangle wave piezo excitation. The data show the lattice constant which is calculated for different scan sizes assuming a constant piezo calibration value of 30.785 nm/V. This apparent lattice constant can be used to correct the piezo calibration value so that the apparent lattice constant can be brought into agreement with the literature value of 0.3161 nm for MoS$_2$ at any particular scan size. The decreasing apparent lattice constant with increasing scan size is consistent with the expected quadratically increasing piezo displacement with excitation voltage. It can be seen from the error bars that the dependence on scanning frequency between 0.5 and 5 Hz is small. The data were well-fit by a quadratic trendline, which allows for accurate calibration at any scan length between 2.5 nm and 9.2 µm. It can also be seen that an alternative calibration, performed with a combination of image FFTs at small image sizes and a calibration grating at large image sizes, provides a much less precise calibration. Part of the success of this calibration lies in the fact that there is no slow scan direction (i.e. image formation with the “Y” piezo) where creep, sample drift, and other effects limit the accuracy. In practice, of course, most experiments involve forming images where these effects will be present. Nevertheless, this calibration represents a large improvement over popular existing methods without an increase in experimental effort.
Drift Correction

In principle, drift errors can also be corrected in this technique. A drift correction technique is developed here for special situations such as measurements at elevated temperatures where drift correction might become necessary. The drift corrections make use of differences that occur between measured frequencies for the two scanning directions.

In the case of X-drift (i.e. drift in the fast scan direction), drift errors can be perfectly corrected by averaging the measured lattice constant for each of the opposing scanning directions. To see this, consider a drift $v$ in the $+X$-direction and a programmed scanning speed $V$ in the $X$-direction. The calculated and true lattice constants for each of the two scanning directions are, using the geometry of Figure A.2:

$$+X$$

163
Averaging the “Measured a” values for the two directions, one arrives at the real value for “a”

This correction has no effect on error from any Y-drift. However, the error in the calculated lattice constant is much smaller for the same drift rate in the Y-direction as compared to the X-direction. In that case, for a drift rate \( v \) in the +Y direction:

\[
a_{true,+x} = \frac{1}{\sqrt{X_1^*+X_2^*+X_2^2}} = \frac{V + v}{\sqrt{f_1^2 + f_1f_2 + f_2^2}} = \frac{V + v}{(V + v)a^*\cos^2\theta_1 + \cos\theta_1\cos\theta_2 + \cos^2\theta_2}
\]

Measured

\[
a_{measured,+x} = \frac{V}{\sqrt{f_1^2 + f_1f_2 + f_2^2}} = \frac{V}{(V + v)a^*\cos^2\theta_1 + \cos\theta_1\cos\theta_2 + \cos^2\theta_2}
\]

\[\therefore a_{measured,+x} = a_{real} - \frac{v}{(V + v)a^*\cos^2\theta_1 + \cos\theta_1\cos\theta_2 + \cos^2\theta_2}\]

-X

True

\[
a_{true,-x} = \frac{1}{\sqrt{X_1^*+X_2^*+X_2^2}} = \frac{V - v}{\sqrt{f_1^2 + f_1f_2 + f_2^2}} = \frac{V - v}{(V - v)a^*\cos^2\theta_1 + \cos\theta_1\cos\theta_2 + \cos^2\theta_2}
\]

Measured

\[
a_{measured,-x} = \frac{V}{\sqrt{f_1^2 + f_1f_2 + f_2^2}} = \frac{V}{(V - v)a^*\cos^2\theta_1 + \cos\theta_1\cos\theta_2 + \cos^2\theta_2}
\]

\[\therefore a_{measured,-x} = a_{real} + \frac{v}{(V + v)a^*\cos^2\theta_1 + \cos\theta_1\cos\theta_2 + \cos^2\theta_2}\]

Averaging the “Measured a” values for the two directions, one arrives at the real value for “a”

This correction has no effect on error from any Y-drift. However, the error in the calculated lattice constant is much smaller for the same drift rate in the Y-direction as compared to the X-direction. In that case, for a drift rate \( v \) in the +Y direction:
\[ a_{\text{measured}} = a_{\text{real}} - \frac{v^2}{2V\sqrt{V^2 + v^2 a^* \cos^2 \theta_1 + \cos \theta_1 \cos \theta_2 + \cos^2 \theta_2}} \]

Lattice Constant Measurement on Square Lattices

In addition to hexagonal lattices such MoS\textsubscript{2} and graphite, LLM was extended to cover the calculation of square lattices. Measurements identical to those described for the calibration above were performed on single crystal NaCl samples, for which atomic lattice resolution was obtained. Only two stick-slip periodicities are available for calculation on this surface and the equation to calculate the reciprocal lattice constant takes the simple form:

\[ a^* = \sqrt{X_1^*^2 + X_2^*^2} \]
Figure A.6: a) Lattice resolved contact mode AFM image on NaCl(001) surface. b) FFT of time-resolved lateral and normal force traces. Peaks due to stick-slip periodicity are annotated as $f_1$ and $f_2$. It was often the case that stick-slip periodicities could be resolved in both force channels.

Figure A.6a shows a lattice-resolved AFM image of the NaCl surface as well as an FFT of a time-resolved force trace while performing reciprocal scanning on the NaCl surface. The two stick-slip frequencies of interest are clearly resolved. For a linescan size of 100 nm and scan frequency of 1 Hz, using the calibration constant for that scan size determined from Figure A.5, the lattice constant for NaCl was measured to be 0.3992 nm. It is typical for only one of the two
ion types to be resolved in scanning probe studies.\(^{27,28}\) In such a case, the expected lattice constant is 0.3988 nm, in close agreement with the value we measure.

![Graph showing lattice constants](image)

**Figure A.7:** Lattice constants measured on bulk and CVD-grown monolayer MoS\(_2\) by continuous scanning at 500 nm/s across a 50 nm scan length. Data are shown in the order in which they were acquired. After 20 min of scanning to stabilize the piezo trajectory, force data was acquired at 97.7 kHz for 5.369 s and an FFT performed. Twenty sequential FFTs were averaged within the AFM software to create a spectrum for analysis. Error bars are the standard deviation of the lattice constant calculated from at least 5 spectra. The calibration constant of the microscope was adjusted to ensure the first measurement on bulk MoS\(_2\) was centered at the literature value 0.3161 nm.

**Single Point Lattice Strain Measurement**

To demonstrate the utility of the method in single-point lattice strain measurements, LLM was utilized to measure the strain at several specific points on CVD-grown monolayer MoS\(_2\) on a SiO\(_2\) substrate. Similar films have been shown to have an average tensile lattice strain of 0.4-1%,\(^{16,29}\) due to the mismatch in thermal expansion coefficient between the SiO\(_2\) and the MoS\(_2\) and the fact that the samples are grown above 700°C. Due to the symmetry assumptions of LLM, measured strain values assume that the strain is isotropic in the surface plane, which is not generally the case. Nevertheless, Figure A.7 shows the results of strain measurements at three specific points on the CVD MoS\(_2\) (the regions of the MoS\(_2\) flakes are shown in Figure A.8). The lateral resolution of these measurements was 50 nm (as compared to 1 μm for Raman\(^{30}\) and 2 μm for synchrotron-based X-ray diffraction\(^{31}\)). Measurements on bulk MoS\(_2\) were performed
before and after the CVD MoS₂ measurements to confirm that the piezo behavior did not drift during the measurement. The average CVD strain value was found to be 0.83%. This value is within the range of previous measurements.¹⁶,²⁹ The measured strain values also showed lateral inhomogeneity between the three spots. This does not agree with prior results, but to our knowledge this is the first strain measurement in this system with lateral resolution below 1µm, so the soundness of this result cannot be assessed.
Figure A.8: Topographic and friction images of regions on CVD MoS₂ where the lattice strain was measured in Figure A.7: (a)-(b) spot 1, (c)-(d) spot 2, (e)-(f) spot 3. Spots 1 and 2 were taken on different regions of the same flake. Spot 3 was taken near the center of a much larger flake. The 3-pointed star polygons in (e) are regions where a second layer of MoS₂ has grown atop the ML MoS₂. The lattice strain measurements were acquired from a 50 nm linescan at the center of each region, as illustrated by a light blue line of length 50 nm in the center of (a) with an arrow to guide the eye.
To evaluate whether LLM can be extended to allow for 2D lattice constant mapping, a more sophisticated analysis was developed. To validate the accuracy of the method, the measurement of the spatially resolved lattice constant was performed on an HOPG sample, for which the lattice constant at all locations is known \textit{a priori}, allowing for the determination of the absolute error. The method requires the acquisition of a high pixel-density 2D image which is subsequently subdivided to measure the lattice constant in individual subregions. Each subregion force image was redimensioned into a single 1D trace, creating data analogous to the time-resolved data acquisitions discussed above. For the demonstration below, the overall image was 100x100 nm\(^2\), 2048x2048 pixel\(^2\). As alluded to earlier, when the analyzed segment length is reduced, the spikes in the FFT comb structure separate. This unacceptably degrades the frequency resolution, and therefore the accuracy of the measured lattice constant, if the frequency of the most intense spike is used for the stick-slip frequency. To restore accuracy to the measurement, we chose to fit the envelope of the comb structure. This requires knowledge of the functional form of this envelope.

To understand the functional form of the envelope, the stick-slip force trajectory during experimental scans was simulated with a sawtooth wave. To simulate the effect of chaining consecutive lines of an image into a single trace, the sawtooth trace was periodically phase shifted by a constant. This produces an FFT with a series of spikes whose amplitudes can be well-fit by a Sinc function, regardless of the phase shifts involved when chaining the traces together.
Figure A.9: a) Simulated stick-slip force trace with a periodic phase shift \(0.3 \times 2\pi\) b) FFT of simulated force traces with periodic phase shifts of various amplitudes. In all cases, the resulting spikes are well fit by a Sinc function.

By simulating a continuous sawtooth wave with periodic phase shifts, it was determined that the appropriate fitting function for the FFT was:

\[ F(f) = y_{\text{off}} + A \text{abs}(\text{sinc}(T(f - f_0))) \]

where \(y_{\text{off}}\) is a y-offset to account for the background intensity, \(A\) is the amplitude of the envelope, \(T\) is the inverse of the segment length, which is known, and \(f_0\) is the stick-slip
frequency of interest. An identical functional form can be found in the pulsed wave radar literature, where a rectangular pulse train signal bears some similarities to the stick-slip signal here.\textsuperscript{32}

To accomplish the fitting, a program was written in IgorPro (Wavemetrics, Portland, OR, USA) that automatically extracts the position and amplitude of each of the FFT spikes across a specified range corresponding to each of the stick-slip frequencies and fits them with the sinc equation given above. This program also generated additional data points to improve the fit by analyzing the same subregion, but with the order in which the scan lines are stitched together reversed. Because this changes the phase shift between subsequent scan lines, the positions of the FFT spikes change. The IgorPro program is included at the end of this Appendix. An example of the fitting results is shown in Figure A.10a for an image of HOPG. The stick-slip frequency shifts between subsequent subregions are due to piezo hysteresis.
To convert the measurement into an accurate lattice constant measurement, given the hysteresis in the piezo trajectory, identical reference measurements on a bulk MoS$_2$ sample were performed before and after the HOPG measurement. Since the lattice constant of the bulk MoS$_2$ is known, the apparent lattice constant measured on the MoS$_2$ for each of the subregions

Figure A.10: a) Example fitting of the lateral force FFT to determine the stick-slip frequency for three sequential subregions of a 100x100 nm$^2$ image of HOPG which has been subdivided into 8x8 equal regions. b) Map of the lattice constants determined for the HOPG image in (a). Each subregion is 12.5 nm square. c) The same data as in (b). The green envelope is the standard deviation of the data. The red envelope is the absolute error of the measurement determined by repeating the measurement 4 times. The dotted line is at the true lattice constant for HOPG.

MoS$_2$ is known, the apparent lattice constant measured on the MoS$_2$ for each of the subregions
could be used to correct the HOPG lattice constants for piezo hysteresis. When this was done, the map shown in Figure A.10b could be generated, with a color scale spanning 1% of the true lattice constant. Figure A.10c clearly demonstrates that the relative error between subregions within the map was very small with a standard deviation of 0.06%. To determine the absolute error that could be expected from lattice constant measurement such as this, the entire procedure was repeated four times. The standard deviation of the absolute error (deviation from the HOPG literature value of 0.2461 nm) for these measurements was 0.19%.

Extension to Piezo Sin Oscillation

While most AFM work is done using triangle wave piezo excitation to allow for image formation, there are techniques such as lateral stiffness measurement and circle scanning which require knowledge of the absolute lateral displacement amplitude of a high frequency sin wave piezo excitation. Accurate knowledge of this parameter is difficult to achieve, given the dependence of piezo trajectories on scanning frequency and excitation amplitude. To address this calibration difficulty, LLM was extended to the case of sin piezo oscillations. Measurements were performed identically to the time resolved measurements discussed above, except with a sin wave oscillation. Since the tip speed is not constant during the sin oscillation, the FFT does not show discrete peaks corresponding to the stick-slip frequency, however, there are two periods of near-constant speed during each oscillation cycle, which provides a recognizable peak in the FFT. If the stick-slip frequency at the maximum speed during the oscillation can be ascertained from the FFT, calculating the amplitude of the piezo oscillation is straightforward (a derivation follows the reference section):

\[
Amplitude = \frac{f_{FFT}}{2\pi f_{osc} \xi_{latt}}
\]

where \(f_{FFT}\) is the stick-slip frequency obtained from the FFT, \(f_{osc}\) is the oscillation frequency of the piezo excitation, and \(\xi_{latt}\) is the spatial frequency of the lattice in the scanning direction. \(\xi_{latt}\) must be determined from an image FFT or standard LLM with a triangle wave excitation.

Simulations of the force signal expected for a sinusoidal oscillation above a periodic surface lattice were performed and the results Fourier transformed. The results are shown in Figure
A.11a. The blue line represents the true frequency of the stick-slip at the maximum tip speed during oscillation. The slight underestimate (0.5-3.5% for amplitudes of 2-20 nm) of the true stick slip frequency will lead to a similar underestimate of the oscillation amplitude. This error could be corrected by performing simulations similar to Figure A.11a for the experimental parameters to determine a correction factor for the experimental data. Figure A.11b shows an FFT of an experimental force trace during a sinusoidal oscillation of 23 nm amplitude and 50 Hz on natural MoS$_2$. Aside from the presence of multiple peaks ($f_2$ and $f_3$) due to slips across each of the close-packed directions, the FFT is qualitatively similar to the simulated result. Figure A.11c shows calibration curves calculated using the above equation for oscillations at multiple amplitudes and 50 or 500 Hz. For comparison, calibration estimates are provided from a cruder method of counting visible slips in the raw force traces near the maximum tip speed for oscillation frequencies of 50, 500, and 5000 Hz. It is immediately apparent that there is a strong decreasing trend of displacement amplitude with frequency. This is a consequence of hysteresis in the piezoelectric actuators. There is no clear precedent for the sublinear dependence on excitation voltage at the higher frequencies indicating a decreasing ferroelectric susceptibility.
We hypothesize that this non-linearity is due to intrinsic effects on the ferroelectric response that have been found to cause a decreasing susceptibility with small, increasing electric fields.\textsuperscript{38} By projecting the fitting curves back to zero excitation, the amplitudes of sub-nm excitations can be accurately calibrated, which is a required for some oscillation techniques, such as the lateral stiffness measurement.\textsuperscript{33}

\[ \text{Force}(t) = \sin \left( \frac{3 \text{ slip}}{\text{nm}} \cdot 2\pi \cdot 5\text{nm} \cdot \sin[50\text{Hz} \times 2\pi \times t] \right) \]

Figure A.11: a) FFT of simulated force trace generated from listed equation which simulates a 5 nm, 50 Hz sin oscillation on a material with a lattice periodicity of 3 nm\textsuperscript{-1}. b) Experimental FFT of lateral force trace on natural MoS\textsubscript{2} while oscillating tip at 50 Hz with amplitude calculated to be 23 nm. \( f_1 \) is identified on the basis of lattice symmetry. c) Calibration curves for sin oscillation technique at 50 and 500 Hz. Estimates of the amplitude based on counting slips for 50, 500, 5000 Hz are included for reference. Data are fit with quadratic functions.
**Discussion**

The compilation of techniques developed here present useful calibration methods for open loop scanning probe microscopes. In particular, the ability to calibrate various lengthscales equally well without substantial additional effort will be useful. The limited variety of commercial calibration gratings typically used for this purpose, particularly for the sub-\(\mu\)m lengthscale, creates difficulty. Calibration by taking FFTs of atomically-resolved crystal lattice images can only be performed on the tens of nm lengthscale before the calibration becomes extremely time-consuming and data-intensive, as well as increasing the degree of tip wear.

The lattice constant mapping technique discussed above could prove useful for mapping strain on atomically resolved lattices presuming the lattice strains are predominantly isotropic. In cases where strains are substantially non-isotropic the symmetry assumptions of LLM breaks down. For the spot mapping of lattice strain on monolayer CVD MoS\(_2\), we attribute our success to the fact that the tensile strain is expected to be reasonably isotropic and that the measurement sampled a 50nm long region which averaged out local strain orientations. A natural extension of LLM to strengthen the strain mapping capability would be to perform scans in two perpendicular directions over the same region. This would allow for the construction of high resolution 2D FFTs for arbitrary crystalline lattices and thereby unambiguously measure arbitrary local strain states. Scanning along the axis of the cantilever beam is problematic in contact mode AFM due to the convolution of normal and buckling forces in the normal force signal channel and satisfactory measurements could not be achieved. No such limitation exists for non-contact scanning probe techniques however. Another strategy to improve the technique would be to reduce the non-linearity of the piezo response. While we have outlined a workable strategy to compensate for hysteresis, the signal-to-noise ratio of the force signal is improved as piezo linearity, and therefore the periodicity of the force signal, also improves. It is in fact possible to essentially eliminate hysteresis by exciting the piezo with a controlled quantity of electric charge, rather than controlling the excitation voltage.\(^{39}\)

The feasibility of LLM in general relies on the precision and long-time stability of the piezoelectric behavior of the AFM scanner. In some ways, the RHK AFM is a uniquely adverse testbed for the technique. Coarse positioning, retract, and approach operations are all
implemented via an inertial drive system which requires the scanner piezos to instantaneously cross their full range of motion repeatedly at high frequency. Nevertheless, after 20 min of stabilization time before making measurements, the piezo trajectories were repeatable enough that high absolute accuracy could be demonstrated for a variety of lattice constant measurements. This implies that other microscope designs could demonstrate even better performance, especially if piezos can be dedicated to making these measurements alone and are decoupled from other positioning operations.

Conclusions

This study demonstrates that individual linescans possess sufficient information to index and measure the lattice constant of crystalline surface lattices with a degree of accuracy unprecedented in the scanning probe literature. This allows for the fast calibration of piezo lateral displacements at arbitrary lengthscales with high accuracy and no need for additional instrumentation or specialized samples aside from a widely available reference sample such as HOPG, NaCl, or natural MoS$_2$. LLM also allows for the accurate measurement of lattice strain with high lateral resolution, as was demonstrated in the case of monolayer CVD MoS$_2$. LLM was demonstrated on the square lattice of NaCl. 2D mapping of the lattice constant with accuracy as high 0.2% was also demonstrated for the case of a symmetric lattice. Finally, a calibration technique for determining the displacement of small sinusoidal oscillation down to the sub-nm lengthscale is demonstrated which can be useful to improve the accuracy of some oscillation-based measurements.

References


(22) Aketagawa, M.; Takada, K. Correction of Distorted STM Image by Using a Regular Crystalline Lattice and 2D FFT. *Nanotechnology* 1995, 6 (4), 105.


**Igor Implementation Code**

The codes used for the analysis of force images to measure the spatially resolved lattice constant are included below. These codes were used in IgorPro v7 to process ASCII data files produced by Gwyddion. `processforceimages2()` divides the four force images (normal and lateral forces, 2 scanning directions) in ASCII format into subregions for further analysis. `CalculateLattice3()` calculates the lattice constant of each subregion based on the spectra output by `processforceimages2()`. These codes are specific to hexagonal lattices where all three stick-slip frequencies are well-resolved, but may be modified in the case of other lattice symmetries or when only a subset of stick-slip frequencies are well-resolved.

```plaintext
function processForceImages2(scaledwave,d)    //Divides large image into subregion spectra suitable for further processing
String scaledwave
variable d
```

181
variable \( n = 1, m = 1, c, k = 1, a = 1 \)

Wave

yourwaveLFL = ::$(scaledwave+"_LFL"), yourwaveLFR = ::$(scaledwave+"_LFR")

Wave

yourwaveNFL = ::$(scaledwave+"_NFL"), yourwaveNFR = ::$(scaledwave+"_NFR")

String LFL = "LFL", LFR = "LFR", NFL = "NFL", NFR = "NFR", img

// LFL = lateral force left, NFR = normal force right, etc.

// clean the data folder first

Variable \( x = 0 \)

Prompt \( x, \) "Kill Waves? (1 if yes, 0 if no)"

DoPrompt "Kill Waves?", x

if (x==1)
    KillWaves/A
endif

FFT/OUT=3/WINF=Hanning/DEST=LFL_FFT yourwaveLFL         // basic
magnitude image FFT - LFL, useful for finding ~stick slip frequencies

FFT/OUT=3/WINF=Hanning/DEST=NFL_FFT yourwaveNFL         // basic
magnitude image FFT - NFL

// Make waves for analysis - LFL

Duplicate yourwaveLFL $(scaledwave+"_LFL_invert")

wave LFL_invert = $(scaledwave+"_LFL_invert")

LFL_invert = yourwaveLFL[q][p]

Duplicate LFL_invert $(scaledwave+"_LFL_1D")

Redimension/N=4194304 $(scaledwave+"_LFL_1D")       // specific to this
image i.e. 2048x2048

FFT/OUT=3/WINF=Hanning/DEST=$(scaledwave+"_LFL_1D_FFT")

$(scaledwave+"_LFL_1D")

// Make waves for analysis - LFR

Duplicate yourwaveLFR $(scaledwave+"_LFR_invert")

wave LFR_invert = $(scaledwave+"_LFR_invert")

LFR_invert = yourwaveLFR[q][p]

Duplicate LFR_invert $(scaledwave+"_LFR_1D")
Redimension/N=4194304 $(scaledwave+"_LFR_1D") //specific to this image i.e. 2048x2048
FFT/OUT=3/WINF=Hanning/DEST=$(scaledwave+"_LFR_1D_FFT")
$(scaledwave+"_LFR_1D")

//Make waves for analysis - NFL - low frequency stick-slip often better resolved in normal force due to force projection along cantilever axis
Duplicate yourwaveNFL $(scaledwave+"_NFL_invert")
wave NFL_invert = $(scaledwave+"_NFL_invert")
NFL_invert = yourwaveNFL[q][p]
Duplicate NFL_invert $(scaledwave+"_NFL_1D")
Redimension/N=4194304 $(scaledwave+"_NFL_1D") //specific to this image i.e. 2048x2048
FFT/OUT=3/WINF=Hanning/DEST=$(scaledwave+"_NFL_1D_FFT")
$(scaledwave+"_NFL_1D")

//Make waves for analysis - NFR
Duplicate yourwaveNFR $(scaledwave+"_NFR_invert")
wave NFR_invert = $(scaledwave+"_NFR_invert")
NFR_invert = yourwaveNFR[q][p]
Duplicate NFR_invert $(scaledwave+"_NFR_1D")
Redimension/N=4194304 $(scaledwave+"_NFR_1D") //specific to this image i.e. 2048x2048
FFT/OUT=3/WINF=Hanning/DEST=$(scaledwave+"_NFR_1D_FFT")
$(scaledwave+"_NFR_1D")

//Make flipped waves for analysis - used for additional data points to improve eventual sinc envelope fit
//Make waves for analysis - LFL flip
Duplicate LFL_invert ("flip_"+scaledwave+"_LFL_invert")
wave LFL_invertflip = ("flip_"+scaledwave+"_LFL_invert")
ImageTransform flipCols LFL_invertflip
Duplicate LFL_invertflip ("flip_"+scaledwave+"_LFL_1D")
Redimension/N=4194304 ("flip_"+scaledwave+"_LFL_1D") //specific to this image i.e. 2048x2048
for (a=1; a<5; a+=1)
k=1
    if (a==1)
img = LFL
wave wave2 = LFL_invert

elseif (a==2)
    img = LFR
    wave wave2 = LFR_invert

elseif (a==3)
    img = NFL
    wave wave2 = NFL_invert

elseif (a==4)
    img = NFR
    wave wave2 = NFR_invert

endif

//loop for each sub-region, normal images, specific to 2048x2048 pixel images
for (n=1; n<d+1; n+=1)
    for (m=1; m<d+1; m+=1)
        c=2048/d
        Make/O/N=(c,c) $(scaledwave+img+"_"+num2str(k))
        wave wave3 = $(scaledwave+img+"_"+num2str(k))
        wave3 = wave2[p+(m-1)*2048/d][q+(n-1)*2048/d]
        SetScale/P x 0,0.0488519785051295,"nm",
        $(scaledwave+img+"_"+num2str(k));DelayUpdate //specific to 100x100nm^2 image
        SetScale/P y 0,0.0488519785051295,"nm",
        $(scaledwave+img+"_"+num2str(k)) //specific to 100x100nm^2 image

        FFT/COLS/DEST=$(scaledwave+img+"_"+num2str(k)+"_FFT")
        $(scaledwave+img+"_"+num2str(k)) //COLS since using the inverted image
        //Now sum the columns
        WaveTransform magnitude
        $(scaledwave+img+"_"+num2str(k)+"_FFT")
Rename M_Magnitude, \( \$(\text{scaledwave}+\text{img}+"\_"+\text{num2str}(k)+"\_FFT\_mag}) \)

\[
\text{wave} \quad \text{wave4} = \quad \$(\text{scaledwave}+\text{img}+"\_"+\text{num2str}(k)+"\_FFT\_mag})
\]

\[
\text{SumDimension/D=1/Y=}-1/\text{DEST}=$\$(\text{scaledwave}+\text{img}+"\_"+\text{num2str}(k)+"\_FFTcols\_sum")
\]

\[
\$(\text{scaledwave}+\text{img}+"\_"+\text{num2str}(k)+"\_FFT\_mag})
\]

SetScale/I \times 0,10.235,\"nm\", \$(\text{scaledwave}+\text{img}+"\_"+\text{num2str}(k)+"\_FFTcols\_sum")

// specific to 100x100nm^2 image

// Convert to 1D and FFT

Duplicate \$(\text{scaledwave}+\text{img}+"\_"+\text{num2str}(k)) \$(\text{scaledwave}+\text{img}+"\_"+\text{num2str}(k)+"\_1D")

variable b = 2048*2048/d/d

Redimension/N=(b) \$(\text{scaledwave}+\text{img}+"\_"+\text{num2str}(k)+"\_1D")

// specific to 100x100nm^2 image

FFT/OUT=3/WINF=\text{Hanning/DEST}=$\$(\text{scaledwave}+\text{img}+"\_"+\text{num2str}(k)+"\_1D\_FFT") \$(\text{scaledwave}+\text{img}+"\_"+\text{num2str}(k)+"\_1D")

KillWaves \$(\text{scaledwave}+\text{img}+"\_"+\text{num2str}(k)), \$(\text{scaledwave}+\text{img}+"\_"+\text{num2str}(k)+"\_FFT") , \$(\text{scaledwave}+\text{img}+"\_"+\text{num2str}(k)+"\_1D")

KillWaves \$(\text{scaledwave}+\text{img}+"\_"+\text{num2str}(k)+"\_FFT\_mag")

k=k+1

endfor

m=1

endfor

endfor

// Process flipped images

for (a=1; a<5; a+=1)

k=1
if (a==1)
    img = LFL
    wave wave2 = LFL_invertflip

elseif (a==2)
    img = LFR
    wave wave2 = LFR_invertflip

elseif (a==3)
    img = NFL
    wave wave2 = NFL_invertflip

elseif (a==4)
    img = NFR
    wave wave2 = NFR_invertflip
endif

//loop for each sub-region, flipped images
for (n=1; n<d+1; n+=1)
    for (m=1; m<d+1; m+=1)
        c=2048/d
        Make/O/N=(c,c)
        "flip_"+scaledwave+img+"_"+num2str(k))
        wave wave3 = "flip_"+scaledwave+img+"_"+num2str(k))
        wave3 = wave2[p+(m-1)*2048/d][q+((d-1)-(n-1))*2048/d]
        SetScale/P x 0,0.0488519785051295,"nm", "flip_"+scaledwave+img+"_"+num2str(k)); DelayUpdate // specific to 100x100nm^2 image
        SetScale/P y 0,0.0488519785051295,"nm", "flip_"+scaledwave+img+"_"+num2str(k))
        // specific to 100x100nm^2 image
        FFT/COLS/DEST="flip_"+scaledwave+img+"_"+num2str(k)+"_FFT")
        "flip_"+scaledwave+img+"_"+num2str(k)) // COLS since using the inverted image
        // Now sum the columns
WaveTransform magnitude

$\text{"flip_{"}scaledwave+img+\text{"}_"+num2str(k)+"_FFT"}$

Rename

M_Magnitude,$(\text{"flip_{"}scaledwave+img+\text{"}_"+num2str(k)+"_FFT_mag"})$

wave wave4 =

$\text{"flip_{"}scaledwave+img+\text{"}_"+num2str(k)+"_FFT_mag"}$

SumDimension/D=1/Y=-1/DEST=$(\text{"flip_{"}scaledwave+img+\text{"}_"+num2str(k)+"_FFTcols_sum"})$

$\text{"flip_{"}scaledwave+img+\text{"}_"+num2str(k)+"_FFT_mag"}$

SetScale/I x 0,10.235,"nm",

$\text{"flip_{"}scaledwave+img+\text{"}_"+num2str(k)+"_FFTcols_sum"}$

//this image

//Convert to 1D and FFT

Duplicate

$\text{"flip_{"}scaledwave+img+\text{"}_"+num2str(k)}$

$\text{"flip_{"}scaledwave+img+\text{"}_"+num2str(k)+"_1D"}$

//variable b = 2048*2048/d/d

Redimension/N=(b)

$\text{"flip_{"}scaledwave+img+\text{"}_"+num2str(k)+"_1D"}$

//this image

FFT/OUT=3/WINF=Hanning/DEST=$(\text{"flip_{"}scaledwave+img+\text{"}_"+num2str(k)+"_1D_FFT"})$ $(\text{"flip_{"}scaledwave+img+\text{"}_"+num2str(k)+"_1D"})$

KillWaves

$(\text{"flip_{"}scaledwave+img+\text{"}_"+num2str(k)})$, $(\text{"flip_{"}scaledwave+img+\text{"}_"+num2str(k)+"_FFT"})$

KillWaves

$(\text{"flip_{"}scaledwave+img+\text{"}_"+num2str(k)+"_1D"})$

KillWaves wave4

k=k+1

endfor

m=1

endfor

endfor

//Clean up unneeded waves
function CalculateLattice3(basename, basename2, d, g, f1, f2, f3, f4, f5, f6, p, s)
    // x&y subregions, fn's are boundaries for peak search chosen by
    // examination of FFTs for approximate locations of each stick-slip peak
    // p=segment width e.g.
    // 256 points * 0.0610426 nm/point = 15.6269056 nm for 32 segments in
    // 100x100 nm^2, 2048x2048 pixel^2 image
    string basename, basename2

    // "s" is search envelope for 2ndary peaks
    variable d, g, f1, f2, f3, f4, f5, f6, p, s
    variable c, e, f, n, q
    String c1, c2  // added for constraint fitting

    c=d*g
    Make/O/N=(c,8) $(basename+_latticecalcs3) wave latticecalcs = $(basename+_latticecalcs3)

    for (n=1; n<c+1; n+=1)
        Wave wave1D = $(basename+_num2str(n)+_1D_FFT) wave1DNFL = $(basename2+_num2str(n)+_1D_FFT)

        Wave flipwave1D = $("flip_"+basename+_num2str(n)+_1D_FFT) flipwave1DNFL = $("flip_"+basename2+_num2str(n)+_1D_FFT)
        Make/O/N=10 $(basename+_num2str(n)+_PeaksX1) Make/O/N=10 $(basename+_num2str(n)+_PeaksY1)
Wave peaksX1 = $(basename+"_"+num2str(n)+"_PeaksX1")
Wave peaksY1 = $(basename+"_"+num2str(n)+"_PeaksY1")
Make/O/N=10 $(basename+"_"+num2str(n)+"_PeaksX2")
Make/O/N=10 $(basename+"_"+num2str(n)+"_PeaksY2")
Wave peaksX2 = $(basename+"_"+num2str(n)+"_PeaksX2")
Wave peaksY2 = $(basename+"_"+num2str(n)+"_PeaksY2")
Make/O/N=10 $(basename+"_"+num2str(n)+"_PeaksX3")
Make/O/N=10 $(basename+"_"+num2str(n)+"_PeaksY3")
Wave peaksX3 = $(basename+"_"+num2str(n)+"_PeaksX3")
Wave peaksY3 = $(basename+"_"+num2str(n)+"_PeaksY3")

WaveStats/Q/R=(f1,f2) wave1DNFL //find peak1, choose correct range for all peaks before running
PeaksX1[2]= V_maxloc
PeaksY1[2]= V_max
q= V_maxloc
WaveStats/Q/R=(q-2/p-s,q-2/p+s) wave1DNFL //make sure these are right i.e. want LFL //make sure p+x, p-x, that x makes sense
PeaksX1[0]= V_maxloc
PeaksY1[0]= V_max
WaveStats/Q/R=(q-1/p-s,q-1/p+s) wave1DNFL
PeaksX1[1]= V_maxloc
PeaksY1[1]= V_max
WaveStats/Q/R=(q+1/p-s,q+1/p+s) wave1DNFL
PeaksX1[3]= V_maxloc
PeaksY1[3]= V_max
WaveStats/Q/R=(q+2/p-s,q+2/p+s) wave1DNFL
PeaksX1[4]= V_maxloc
PeaksY1[4]= V_max
WaveStats/Q/R=(f1,f2) flipwave1DNFL //find peak1, choose correct range for all peaks before running
PeaksX1[5]= V_maxloc
PeaksY1[5]= V_max
q= V_maxloc
WaveStats/Q/R=(q-2/p-s,q-2/p+s) flipwave1DNFL //make sure these are right i.e. want LFL
PeaksX1[6]= V_maxloc
PeaksY1[6]= V_max
WaveStats/Q/R=(q-1/p-s,q-1/p+s) flipwave1DNFL
PeaksX1[7]= V_maxloc
PeaksY1[7]= V_max
WaveStats/Q/R=(q+1/p-s,q+1/p+s) flipwave1DNFL
PeaksX1[8]= V_maxloc
PeaksY1[8]= V_max
WaveStats/Q/R=(q+2/p-s,q+2/p+s) flipwave1DNFL
PeaksX1[9]= V_maxloc
PeaksY1[9]= V_max
q=PeaksX1[2]

Make/D/N=4/O W_coef
c1 = "K1 >" + num2str(q-1/p)
c2 = "K1 < " + num2str(q+1/p)

Make/O/T CTextWave={c1,c2}  //Constrain fit to reasonable values

W_coef[0] = {0.5,q,p*Pi,0.05}  //Specific to the segment width 256*0.0610426*Pi=49.09337 for 32 segs, 7.8134528 nm 64seg

FuncFit/Q/H="0010" syncEnvelope W_coef PeaksY1 /X=PeaksX1 /D/C=CTextWave //added C=CTextWave

e = W_coef[1]
latticecalcs[n-1][0] = e

WaveStats/Q/R=(f3,f4) wave1D  //find peak2
PeaksX2[2]= V_maxloc
PeaksY2[2]= V_max
q= V_maxloc -
Wavestats/Q/R=(q-2/p-s,q-2/p+s) wave1D  //make sure these are right i.e. want LFL
PeaksX2[0]= V_maxloc
PeaksY2[0]= V_max

WaveStats/Q/R=(q-1/p-s,q-1/p+s) wave1D
PeaksX2[1]= V_maxloc
PeaksY2[1]= V_max

WaveStats/Q/R=(q+1/p-s,q+1/p+s) wave1D
PeaksX2[3]= V_maxloc
PeaksY2[3]= V_max

WaveStats/Q/R=(q+2/p-s,q+2/p+s) wave1D
PeaksX2[4]= V_maxloc
PeaksY2[4]= V_max

WaveStats/Q/R=(f3,f4) flipwave1D  //find peak2
PeaksX2[5]= V_maxloc
PeaksY2[5]= V_max
q= V_maxloc -
Wavestats/Q/R=(q-2/p-s,q-2/p+s) flipwave1D  //make sure these are right i.e. want LFL

PeaksX2[6]= V_maxloc
PeaksY2[6]= V_max

WaveStats/Q/R=(q-1/p-s,q-1/p+s) flipwave1D
PeaksX2[7]= V_maxloc
PeaksY2[7]= V_max

WaveStats/Q/R=(q+1/p-s,q+1/p+s) flipwave1D
PeaksX2[8]= V_maxloc
PeaksY2[8]= V_max

WaveStats/Q/R=(q+2/p-s,q+2/p+s) flipwave1D
PeaksX2[9]= V_maxloc
PeaksY2[9]= V_max
q=PeaksX2[2]

Make/D/N=4/0 W_coef

c1 = "K1 >" + num2str(q-1/p)
c2 = "K1 < " + num2str(q+1/p)
Make/O/T CTextWave={c1,c2}  //Constrain fit to reasonable values

W_coef[0] = (0.5,q,p*Pi,0.05)    //Specific to the segment width 256*0.0610426*Pi=49.09337 for 32 segs,
FuncFit/Q/H="0010" syncEnvelope W_coef PeaksY2 /X=PeaksX2
/D=C=CTextWave  //added C=CTextWave
 e = W_coef[1]
latticecalcs[n-1][1] = e

Wavestats/Q/R=(f5,f6) wave1D    //find peak3
PeaksX3[2]= V_maxloc
PeaksY3[2]= V_max
q= V_maxloc
Wavestats/Q/R=(q-2/p-s,q-2/p+s) wave1D    //make sure these are right i.e. want LFL
PeaksX3[0]= V_maxloc
PeaksY3[0]= V_max
Wavestats/Q/R=(q-1/p-s,q-1/p+s) wave1D
PeaksX3[1]= V_maxloc
PeaksY3[1]= V_max
Wavestats/Q/R=(q+1/p-s,q+1/p+s) wave1D
PeaksX3[3]= V_maxloc
PeaksY3[3]= V_max
Wavestats/Q/R=(q+2/p-s,q+2/p+s) wave1D
PeaksX3[4]= V_maxloc
PeaksY3[4]= V_max
Wavestats/Q/R=(f5,f6) flipwave1D    //find peak3
PeaksX3[5]= V_maxloc
PeaksY3[5]= V_max
q= V_maxloc
Wavestats/Q/R=(q-2/p-s,q-2/p+s) flipwave1D    //make sure these are right i.e. want LFL
PeaksX3[6]= V_maxloc
PeaksY3[6]= V_max
Wavestats/Q/R=(q-1/p-s,q-1/p+s) flipwave1D
PeaksX3[7]= V_maxloc
PeaksY3[7]= V_max
Wavestats/Q/R=(q+1/p-s,q+1/p+s) flipwave1D
PeaksX3[8]= V_maxloc
PeaksY3[8]= V_max
Wavestats/Q/R=(q+2/p-s,q+2/p+s) flipwave1D
PeaksX3[9]= V_maxloc
PeaksY3[9]= V_max
q=PeaksX3[2] /
Make/D/N=4/O W_coef

c1 = "K1 >" + num2str(q-1/p)
c2 = "K1 < "+ num2str(q+1/p)
Make/O/T CTextWave={c1,c2}  //Constrain fit to reasonable values
\[ W_{\text{coef}}[0] = \{0.5, q, p^*\pi, 0.05\} \] //Specific to the segment width 256*0.0610426*\pi=49.09337 for 32 segs,

\[
\text{FuncFit/Q/H}="001" \text{ syncEnvelope } W_{\text{coef}} \text{ PeaksY3 /X=PeaksX3} \\
/D/C=CTextWave //added C=CTextWave
\]
e = W_{\text{coef}}[1]
latticecalcs[n-1][2] = e

\[
\begin{align*}
latticecalcs[n-1][3] &= 1/sqrt((latticecalcs[n-1][0])^2+(latticecalcs[n-1][1])^2+(latticecalcs[n-1][2])^2) \\
latticecalcs[n-1][4] &= 1/sqrt((latticecalcs[n-1][1])^2-(latticecalcs[n-1][1])*(latticecalcs[n-1][2])+(latticecalcs[n-1][2])^2) \\
latticecalcs[n-1][5] &= 1/sqrt((latticecalcs[n-1][0])^2-(latticecalcs[n-1][0])*(latticecalcs[n-1][2])+(latticecalcs[n-1][2])^2) \\
latticecalcs[n-1][6] &= (latticecalcs[n-1][3]+latticecalcs[n-1][4]+latticecalcs[n-1][5])/3 //average "a" \\
latticecalcs[n-1][7] &= \max(\text{abs} (latticecalcs[n-1][3]-latticecalcs[n-1][6]), \text{abs} (latticecalcs[n-1][4]-latticecalcs[n-1][6]), \text{abs} (latticecalcs[n-1][5]-latticecalcs[n-1][6]) ) //average "a" \\
\end{align*}
\]

Error

EndFor

end

**Sin wave oscillation**

In the text, an equation for the oscillation amplitude of a sin wave excitation is presented which depends on the stick slip frequency extracted from the FFT of the force trace, the spatial frequency of the lattice in the scanning axis, and the frequency of the tip oscillation. This equation may be derived as follows:

**Idealized waveform of lattice in scanning direction:**

\[ g(x) = \sin 2\pi \xi_{\text{latt}} x \]

where \( x \) is the position coordinate and \( g \) is the amplitude of the surface corrugation.

If \( x(t) \) represents the probe tip and a sinusoidal excitation is applied:

\[ g(t) = \sin 2\pi \xi_{\text{latt}} x(t) = \sin(2\pi \xi_{\text{latt}} A \sin(2\pi f_{\text{osc}} t)) \]

where \( A \) is the amplitude of the sinusoidal tip excitation.
The maximum tip velocity during the cycle is when \( \sin[2\pi f_{osc} t] = 0 \) or when

\[ 2\pi f_{osc} t = n\pi, n = 0,1,2 \ldots \] At this point, the maximum tip speed is:

\[
v = \frac{\delta A \sin[2\pi f_{osc} t]}{\delta t}, t = \frac{n}{2\pi f_{osc}} = 2\pi f_{osc} A \cos 2\pi f_{osc} t, t = \frac{n}{2\pi f_{osc}} = 2\pi f_{osc} A
\]

The frequency of stick – slip at this maximum speed (in the time domain) is:

\[
v \left( \frac{nm}{s} \right) \cdot \xi_{latt} \left( \frac{1}{nm} \right) = f_{slip} \left( \frac{1}{s} \right) = 2\pi f_{osc} A \xi_{latt}
\]

\[
\therefore A = \frac{f_{slip}}{2\pi f_{osc} \xi_{latt}}
\]

In the text, we assume that \( f_{slip} = f_{fft} \) to achieve the final form.

We show, via simulation, that this assumption leads to modest errors.