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The extreme and unusual nanotribological properties of carbon

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The extreme and unusual tribological properties of carbon

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- Macroscale friction and wear: environmental passivation and switching behavior
- Atomic-scale friction of graphene: size (# of layers) matters

A special promotional message

The Nanoprobe Network: http://nanoprobenetwork.org
A free resource for scanning probe microscopists

-Forums for asking and answering SPM questions, including live chats with experts once a month
-Probe-pedia: The user-generated encyclopedia of SPM
-Blogs by scientists in academia and industry
-Shared software, images, video files
-Coming soon: Job listings

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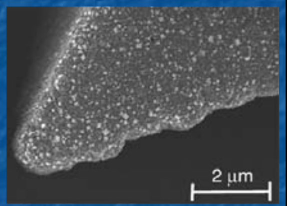
Macroscale friction and wear of ultrananocrystalline diamond (UNCD)

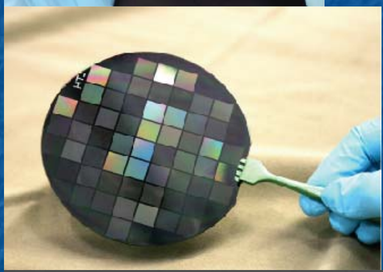
Collaboration with A. Sumant, J. Carlisle, W.G. Sawyer

Tribological Applications of Diamond

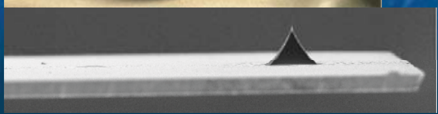
Coatings for mechanical seals



Tools: macro to micro



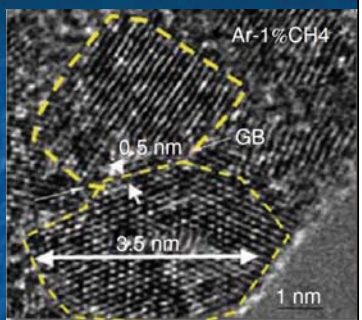
Micro-electro-mechanical systems (MEMS)



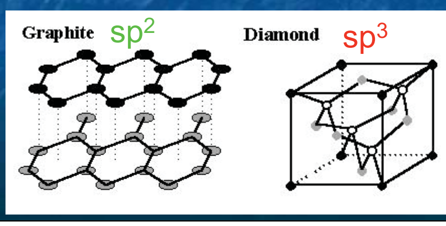
Ultrahigh performance atomic force microscopy (AFM) probes

Ultrananocrystalline diamond (UNCD)

- Growth → Large-area chemical vapor deposition
- Roughness → Small grain size (2-5 nm), low roughness (<8 nm RMS)
- Bonding → Diamond nanograins, with sp^2/sp^3 grain boundaries
- Modulus → Young's modulus ~960 GPa (single crystal diamond: 1050 GPa)
- Hardness → Hardness ~90 GPa (single crystal diamond: 100 GPa)

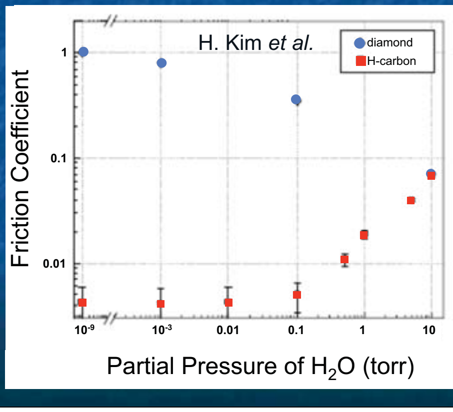


TEM image of UNCD nanograins
Source: Argonne National Labs



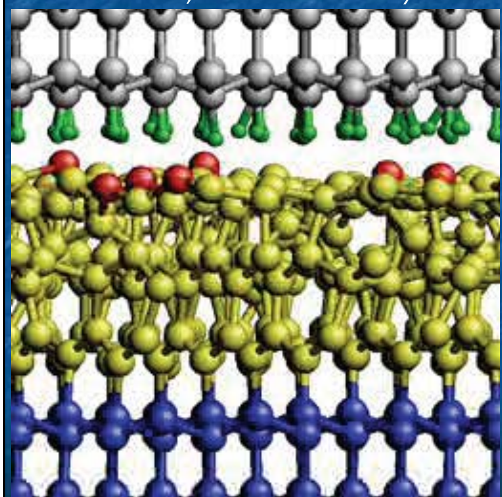
- Challenge: environmental sensitivity
  - *Diamond and hydrogen-free amorphous carbon have low friction if they are smooth and water vapor is present*
  - *amorphous, hydrogen-containing carbon films perform worse when water vapor is present*

- Gardos, *Trib. Lett.* (1999), H. Kim et al., *Trib. Lett.* (2006), and several others
- but *spectroscopic analysis is lacking, and the mechanisms are not understood*



Importance of surface chemistry and bonding at the tribological interface

Classical MD Simulations from J. Harrison, U.S. Naval Academy



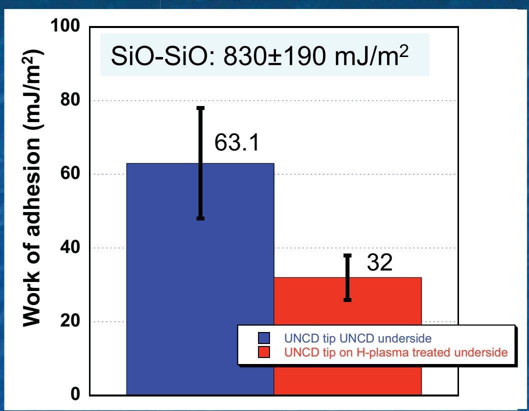
- Contact stresses cause bonds to break, leaving dangling bonds
- Dangling bonds can re-bond across the interface, increasing friction and wear
- H-termination and sp^3 bonding diamond lower adhesion, friction, and wear

green: H
red: initially sp-bonded C
yellow: initially sp^2-bonded C
blue & gray: diamond

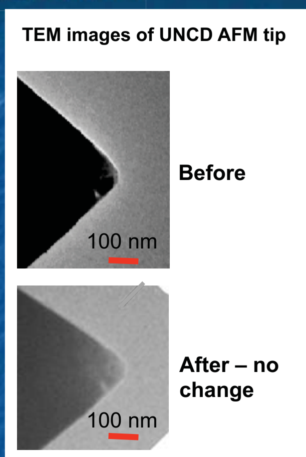
G.T. Gao, P.T. Mikulski, and J. A. Harrison, J. Am. Chem. Soc., Vol. 124, No.24 (2002)

AFM studies of friction and adhesion for UNCD

Nanoscale adhesion at the UNCD:UNCD interface measured with AFM

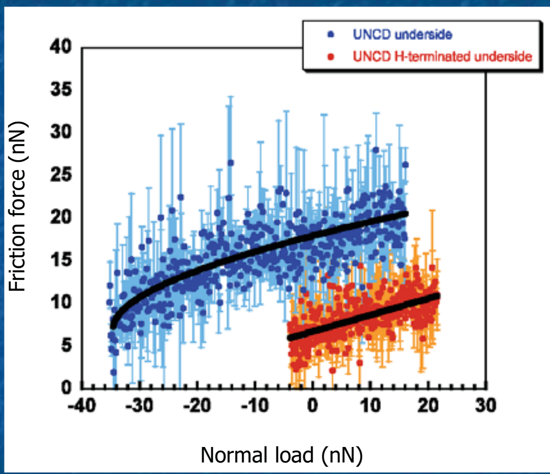


See Sumant *et al*, ***Adv. Mat.*** **2005,** ***PRB*** **2007**



- H-plasma treatment reduces adhesion and friction
- values are consistent with van der Waals interactions
- values consistent with (i.e., slightly larger than) recent DFT calculation by Y. Qi *et al.* (*Surf. Sci.* 2006) and by Zilibotti, Righi, and Ferrario (*PRB 2009)*

Friction measurements were performed with a UNCD AFM tip on UNCD underside surfaces



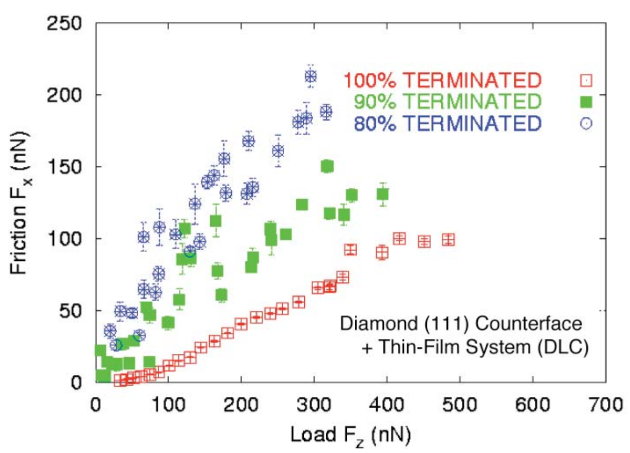
TEM images of AFM tip (UNCD)

Before

After

- H-termination reduces friction and adhesion appreciably

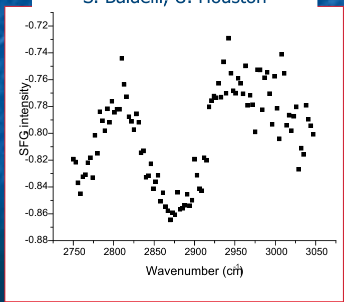
Molecular dynamics also predicts that Hydrogen termination reduces friction

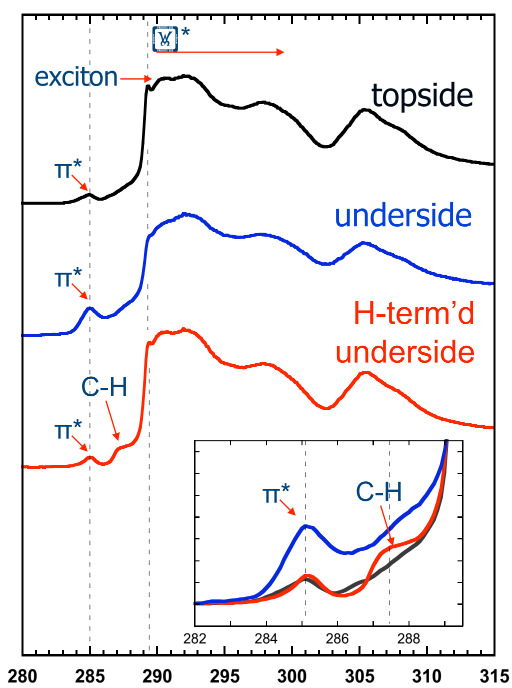


Gao, Mikulski, & Harrison, *J. Am. Chem. Soc.* 124, 7202 (2002).

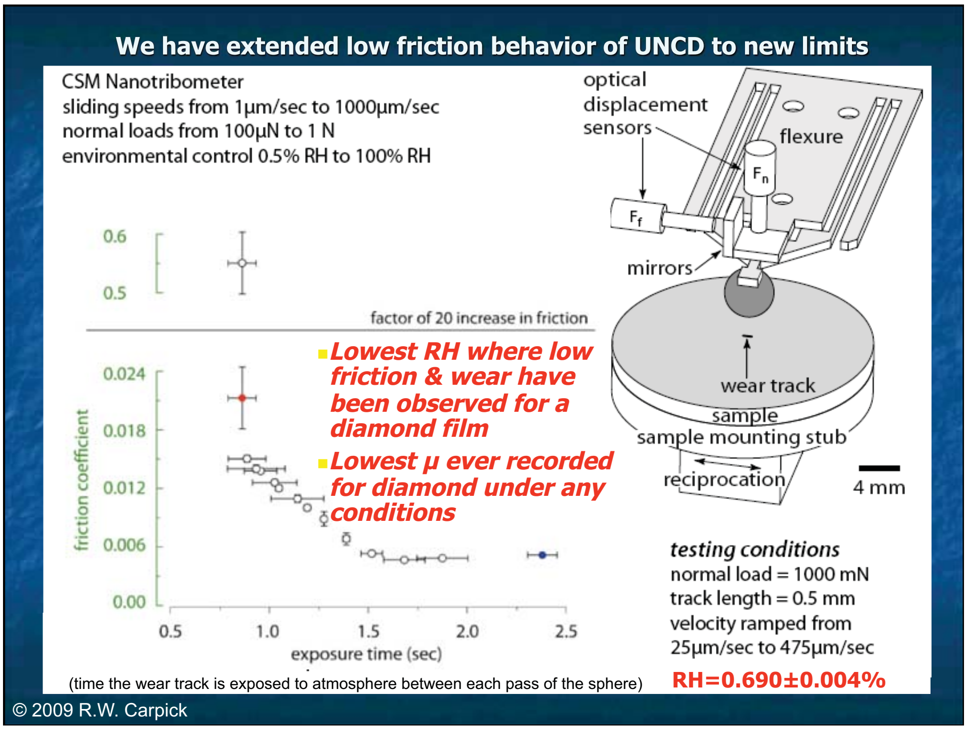
NEXAFS: H-plasma removes sp^2-bonded carbon and contaminants, leaving a H-terminated, sp^3-optimized surface

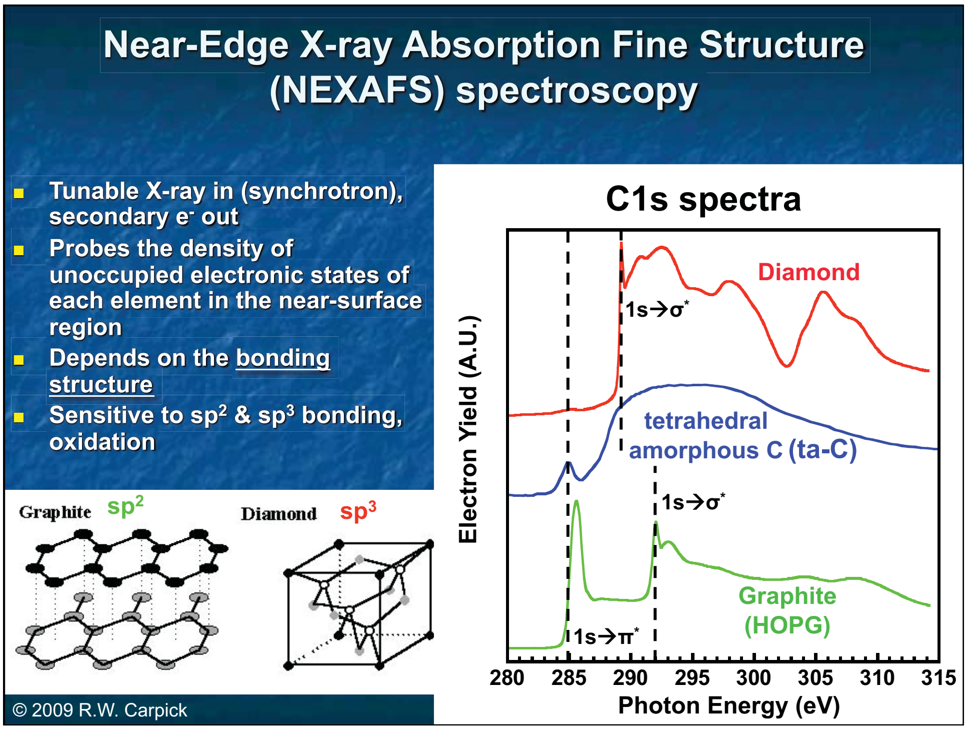
Sum Frequency Generation data
S. Baldelli, U. Houston





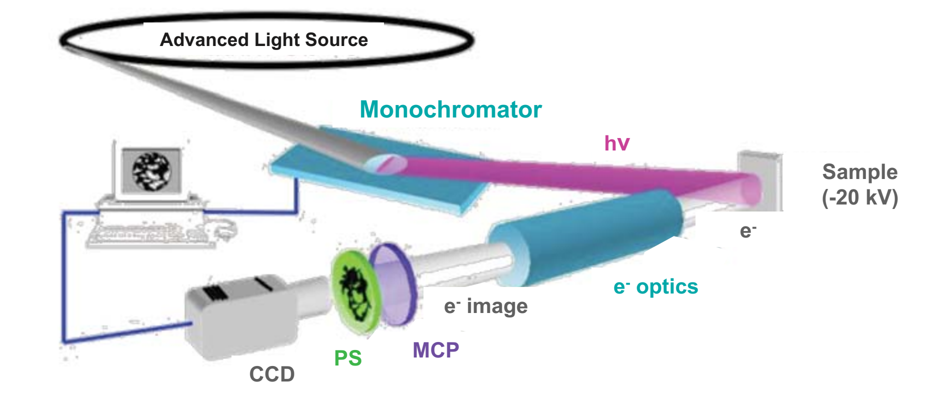
Macro-scale friction and wear of UNCD self-mated interfaces


We have extended low friction behavior of UNCD to new limits
CSM Nanotribometer
sliding speeds from 1μm/sec to 1000μm/sec
normal loads from 100μN to 1 N
environmental control 0.5% RH to 100% RH
optical displacement sensors
flexure
mirrors
wear track
sample
sample mounting stub
reciprocation
4 mm
factor of 20 increase in friction
Lowest RH where low friction & wear have been observed for a diamond film
Lowest μ ever recorded for diamond under any conditions
friction coefficient
exposure time (sec)
0.6
0.5
0.024
0.018
0.012
0.006
0.00
0.5
1.0
1.5
2.0
2.5
testing conditions
normal load = 1000 mN
track length = 0.5 mm
velocity ramped from 25μm/sec to 475μm/sec
(time the wear track is exposed to atmosphere between each pass of the sphere)
RH=0.690±0.004%
© 2009 R.W. Carpick


Near-Edge X-ray Absorption Fine Structure (NEXAFS) spectroscopy
Tunable X-ray in (synchrotron), secondary e- out
Probes the density of unoccupied electronic states of each element in the near-surface region
Depends on the bonding structure
Sensitive to sp2 & sp3 bonding, oxidation
Graphite sp2
Diamond sp3
C1s spectra
Diamond
tetrahedral amorphous C (ta-C)
Graphite (HOPG)
1s→σ*
1s→π*
Electron Yield (A.U.)
Photon Energy (eV)
280
285
290
295
300
305
310
315
© 2009 R.W. Carpick

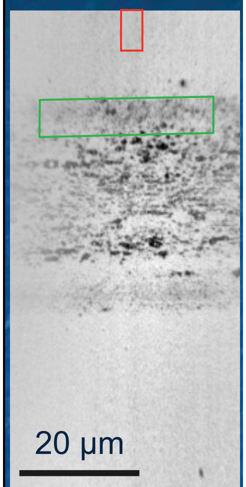
PhotoElectron Emission Microscopy

PEEM schematic:

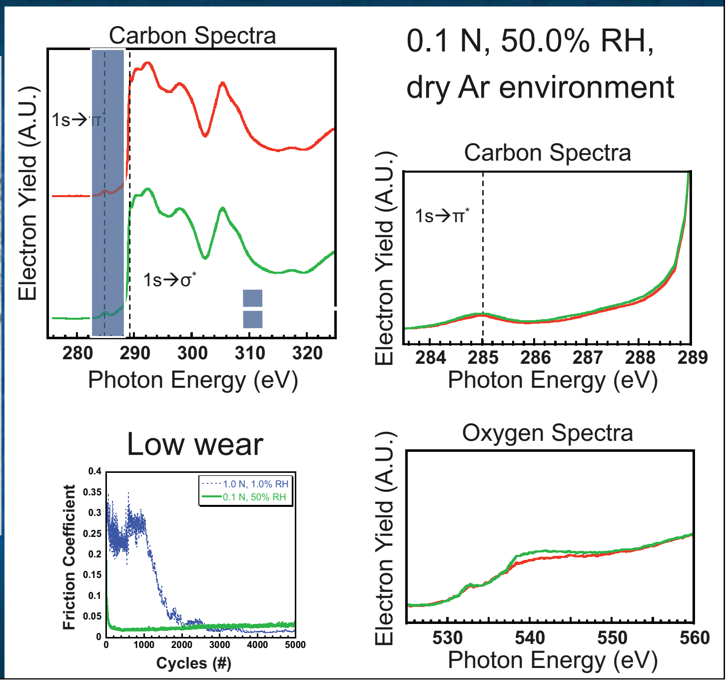


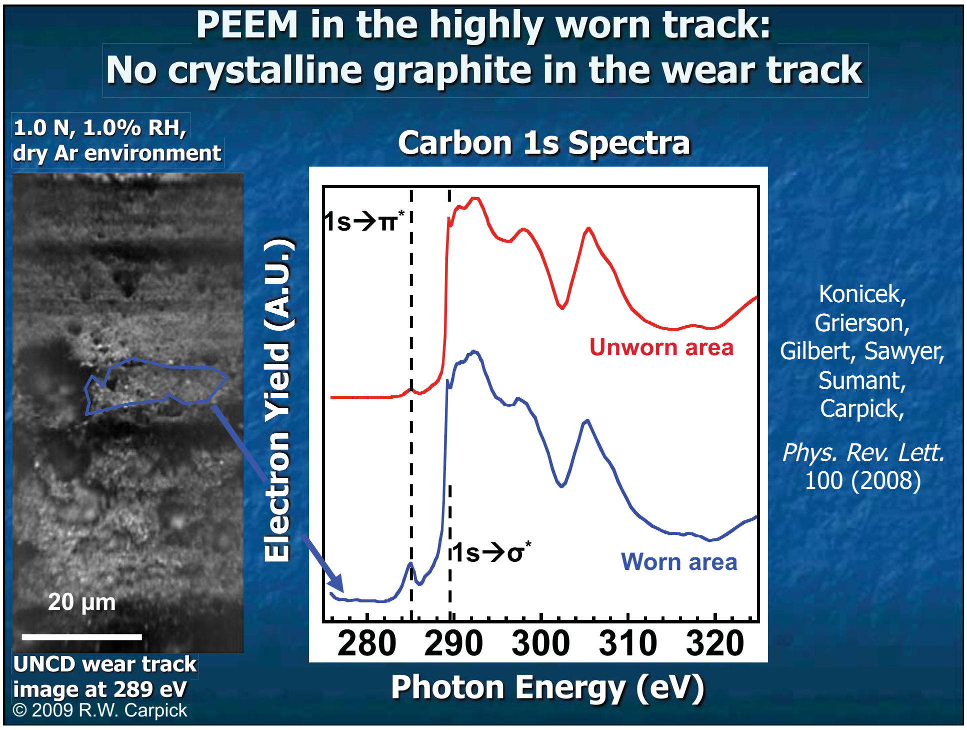
- Spatially sensitive spectroscopic information (down to <50 nm)
- Ideal for *ex situ* wear studies to compare worn and unworn areas

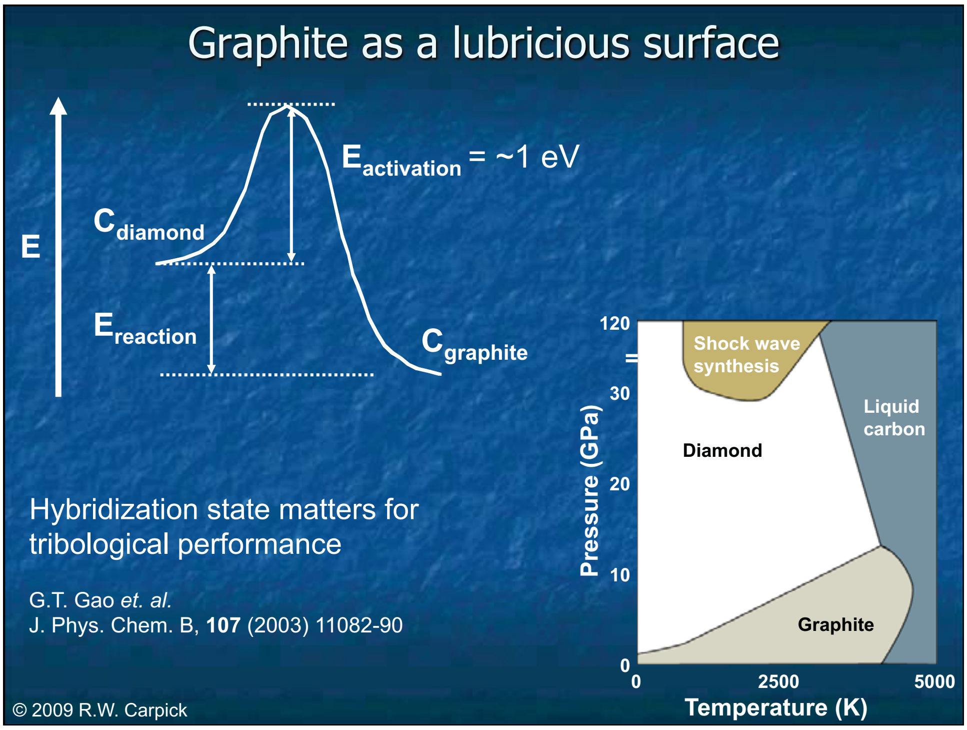
PEEM in the lightly worn track: Virtually no change

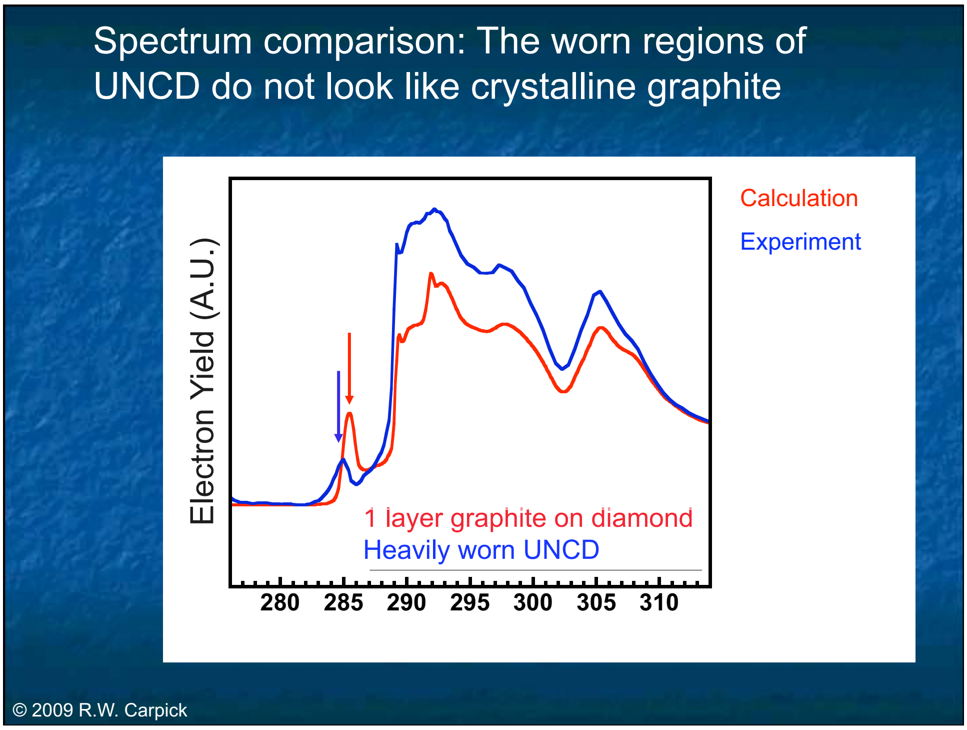


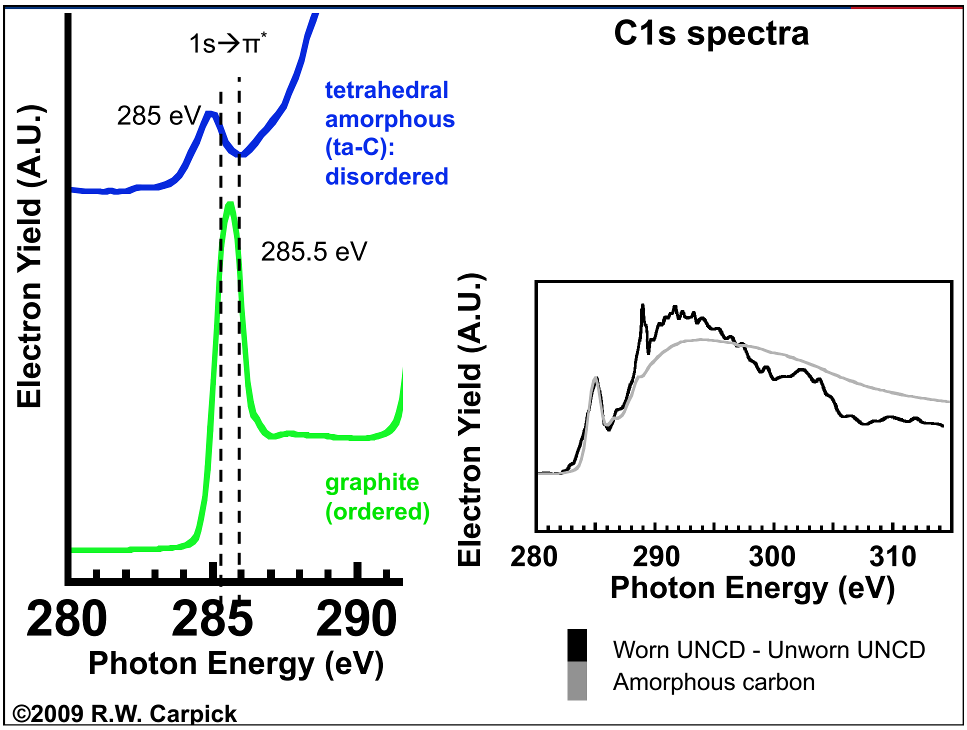
UNCD wear track image at 289 eV

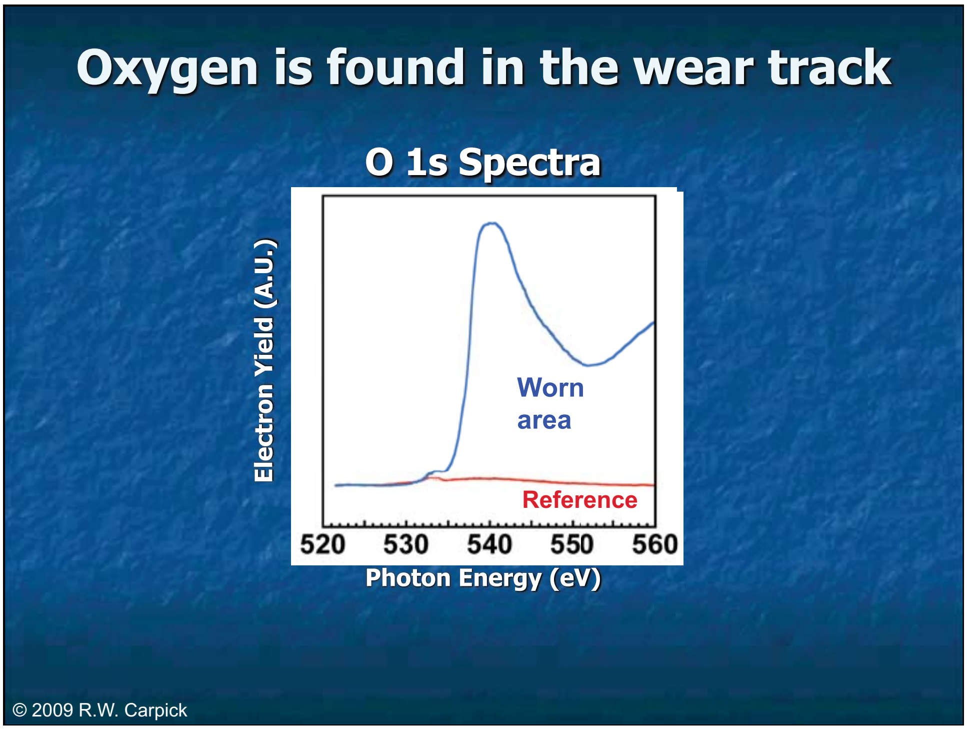


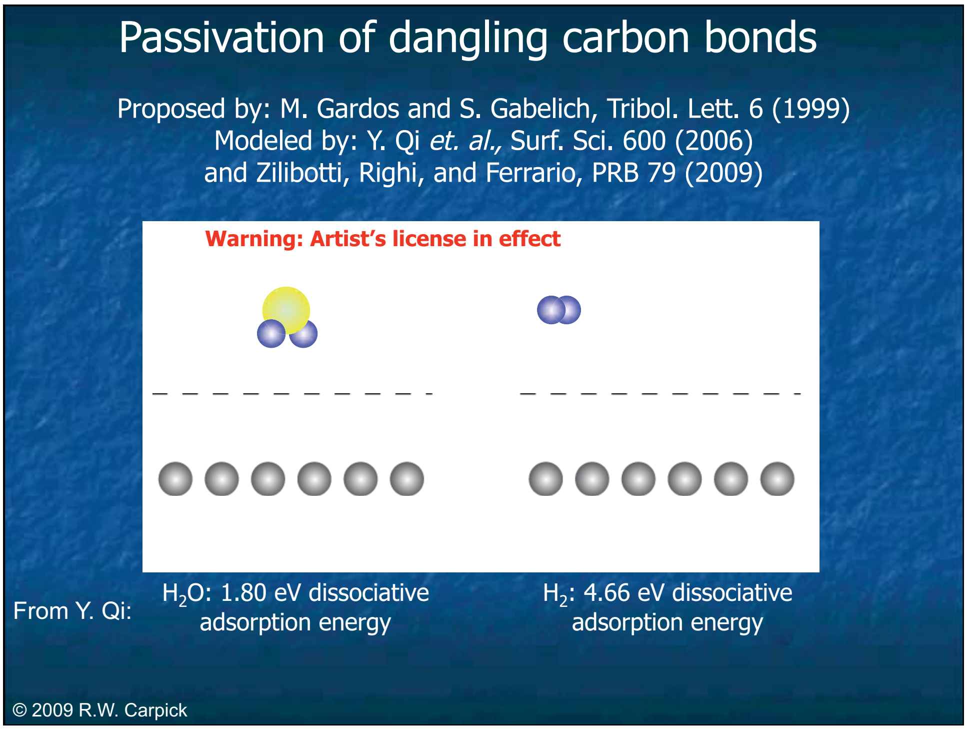

PEEM in the highly worn track:
No crystalline graphite in the wear track
1.0 N, 1.0% RH,
dry Ar environment
Carbon 1s Spectra
1s→π*
1s→σ*
Unworn area
Worn area
Electron Yield (A.U.)
280 290 300 310 320
Photon Energy (eV)
20 µm
UNCD wear track
image at 289 eV
© 2009 R.W. Carpick
Konicek,
Grierson,
Gilbert, Sawyer,
Sumant,
Carpick,
Phys. Rev. Lett.
100 (2008)


Graphite as a lubricious surface
E
E activation = ~1 eV
C diamond
E reaction
C graphite
Hybridization state matters for
tribological performance
G.T. Gao et. al.
J. Phys. Chem. B, 107 (2003) 11082-90
© 2009 R.W. Carpick
Shock wave synthesis
Liquid carbon
Diamond
Graphite
Pressure (GPa)
120
30
20
10
0
0
2500
5000
Temperature (K)


Spectrum comparison: The worn regions of UNCD do not look like crystalline graphite
Electron Yield (A.U.)
Calculation
Experiment
1 layer graphite on diamond
Heavily worn UNCD
280 285 290 295 300 305 310
© 2009 R.W. Carpick


C1s spectra
Electron Yield (A.U.)
1s→π*
285 eV
tetrahedral amorphous (ta-C): disordered
285.5 eV
graphite (ordered)
280 285 290
Photon Energy (eV)
Electron Yield (A.U.)
280 290 300 310
Photon Energy (eV)
Worn UNCD - Unworn UNCD
Amorphous carbon
©2009 R.W. Carpick


Oxygen is found in the wear track
O 1s Spectra
Electron Yield (A.U.)
Worn
area
Reference
520
530
540
550
560
Photon Energy (eV)
© 2009 R.W. Carpick


Passivation of dangling carbon bonds
Proposed by: M. Gardos and S. Gabelich, Tribol. Lett. 6 (1999)
Modeled by: Y. Qi et. al., Surf. Sci. 600 (2006)
and Zilibotti, Righi, and Ferrario, PRB 79 (2009)
Warning: Artist's license in effect
From Y. Qi:
H_2O: 1.80 eV dissociative adsorption energy
H_2: 4.66 eV dissociative adsorption energy
© 2009 R.W. Carpick

Summary of UNCD tribology

- Self-mated UNCD interfaces under rather dry conditions have impressively good performance
  - extremely low friction (down to 0.005 at <1% RH)
- The formation of a crystalline graphite layer is NOT the mechanism of low friction under any conditions tested
  - Some amorphous carbon is found
- Oxidation occurs, particularly under more severe conditions; chemical passivation (by -H, or -OH) is the key
  - there is a dynamic competition between bond breaking (leading to bonding across the interface and wear) and bond passivation by dissociative adsorption (which is clearly feasible from energetics)
  - Leads to rapid switching between low & high friction with a small change in humidity: runaway behavior