In-situ TEM studies of tribo-induced bonding modification in near-frictionless carbon films

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Introduction

- DLC: metastable disordered carbon with significant sp^3 hybridization.
- Properties: high hardness, strength, chemically inert, electrically insulating, optically transparent, low static and kinetic friction.
- Applications: as protective coatings in automotive gears, magnetic storage disks, biological implants, MEMS devices.
- Common Methods: PVD and CVD !

Introduction

- Plasma-enhanced chemical vapor deposition (PECVD) developed by Erdemir *et al.*
- Ultra-low friction hydrogenated films in a plasma of a 3:1 - H_2:CH_4 mixture.
- Friction coefficients as low as 0.001 (dry conditions).
- Named as "near-frictionless carbon" (abbreviated NFC).
- DLCs have the largest range of wear and friction among solid lubricants (μ= 0.001 to >0.5).
- Humidity, hydrogen and oxygen partial pressure affect the friction and wear rates.

Introduction

- Hydrogen-free DLC: low friction in humid conditions.
- Hydrogenated DLC: low friction in dry or inert conditions.
- Hydrogenated DLC: hydrogen termination layer, which has resistance to tribochemical reactions on the surface of NFC films.
- Friction behavior: stabilized by doping with S, Ti, Fe, or Si.
- The presence of third-bodies or transfer layers affect the friction properties of DLC.
- Graphitized transfer layers maintain low and stable friction in humid conditions (just like graphite).

Introduction

- TEM and Raman analysis verified the presence of graphitized debris particles on the surfaces of worn DLC.
- The formation and wear of transfer layers central to the study and understanding of self-lubricating carbon surfaces.

Objective: to reproduce DLC sliding conditions within the TEM and look for direct evidence of mechanically induced formation of a carbon rich transfer layer.

Experimental

- Method: PECVD
- A capacitively coupled r.f. discharge plasma used to deposit films on a substrate.
- 30 mTorr, bias of -500 volts.
- A 30 nm bond layer of Si deposited to improve adhesion to the Cu-grid.
- Carbon film deposited at room temperature: 100 nm.
- NFC6 (1:3::CH_4:H_2) and NFC7 (Pure CH_4).
- NFC7 less favorable tribological performance (high friction and wear).

Experimental

- Sliding element: standard electropolishing techniques (0-5 V AC) from 0.25 mm polycrystalline tungsten (99.995%) wire in a 2 N NaOH solution to a radius of curvature on the order of 10 nm.
- An HS100 STM-Holder™ was used to carry out *in-situ* sliding experiments (designed for a 200KV SFE-TEM).
- Mid-10^{-7} Torr range vacuum / liquid N_2 cooled anti-contamination finger used to check the contamination.
- The nanomanipulation holder configured to accept 3 mm TEM grids at a 30-degree inclination to the horizontal.

Experimental

- A piezo elements based spatially controlled probe, capable of STM measurements was inserted.
- Resolution: 0.2Å in XY and 0.025Å in Z
- Coarse motion: ±1-2 mm in XY and ± 1 mm in Z.
- Sliding was performed after establishing a gentle contact with the sample.
- A track length of a few hundred nanometers at a sliding speed of 1 μm/sec.
- EELS spectra collected every 50-100 passes.

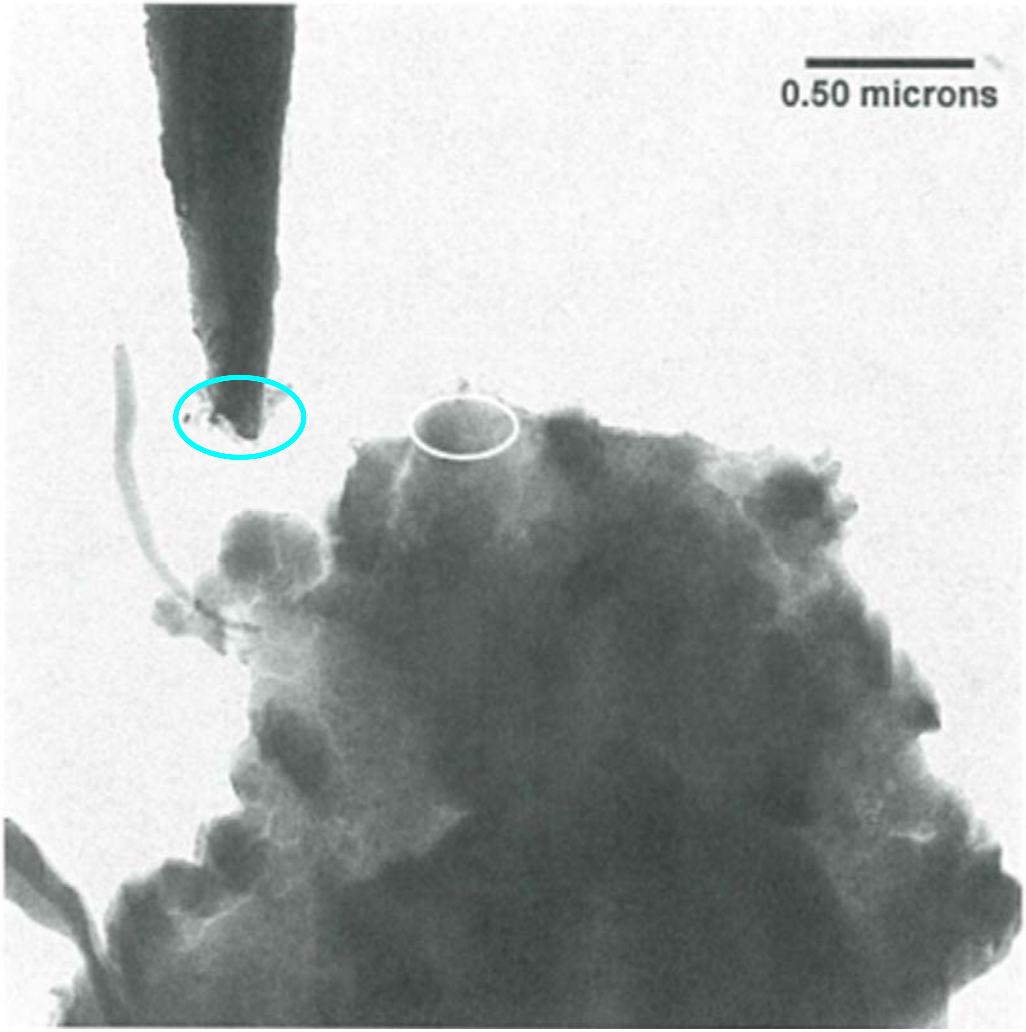
Experimental

- Direct measurement of the magnitude of the normal force applied to the samples could not be done.
- EELS: a post-column Gatan image filter was used to perform EELS measurements. Each spectrum was acquired from a region of approximately 100 nm length.
- TEM: bright field images were taken before and after sliding to record the microstructure of the sample.

Results and Discussion

- Early work:
  - the steady-state coefficient of friction was due to wear-induced graphitization.
  - Sliding velocity and loading level influence the graphitization process.
  - This work was done ex-situ, which may have been affected by humidity, capillary forces, etc.
- Present study: In-situ studies done in high vacuum.

Results and Discussion



Bright field TEM image of NFC6. The white circle shows the sliding region after 200 passes.

Results and Discussion

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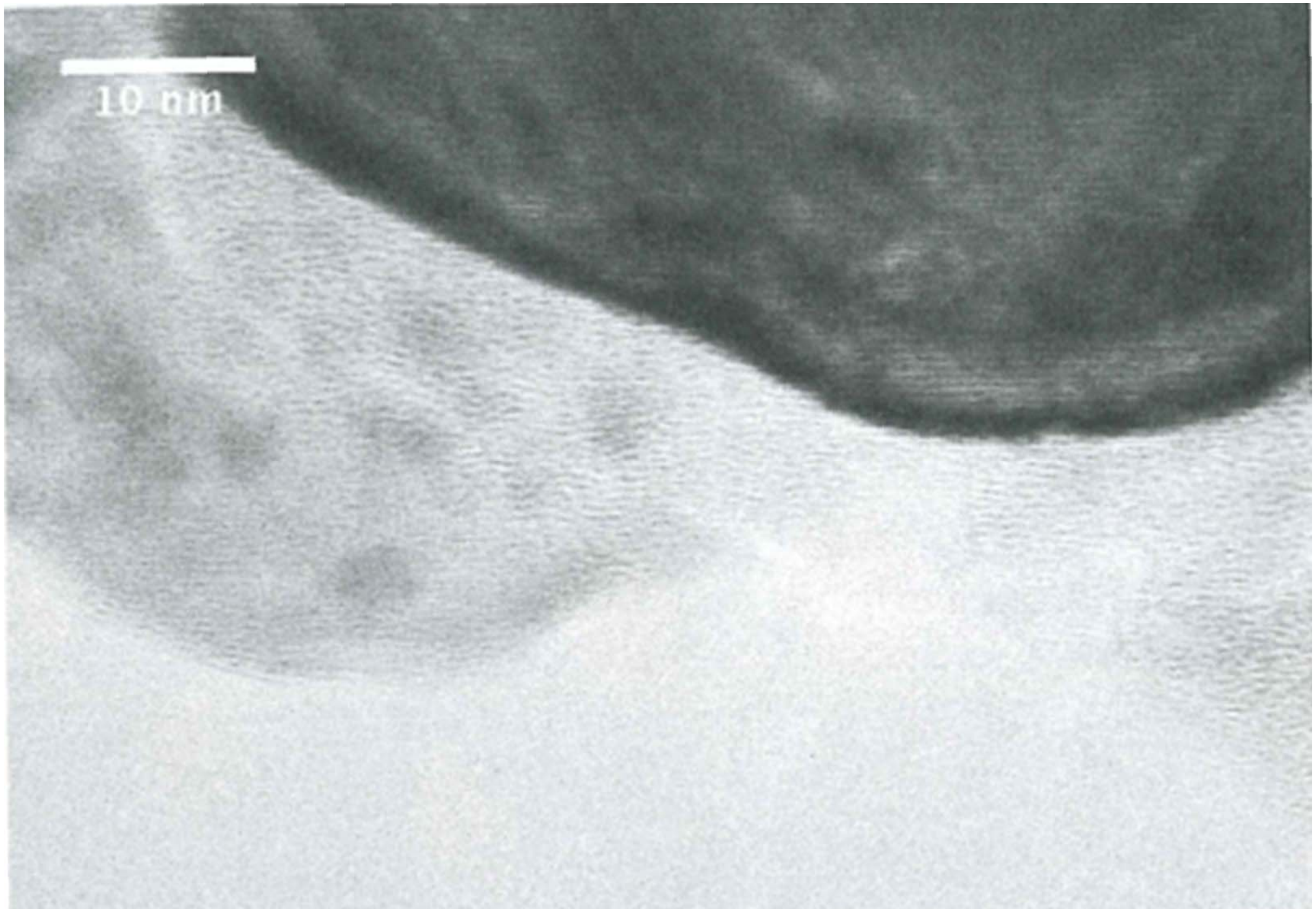


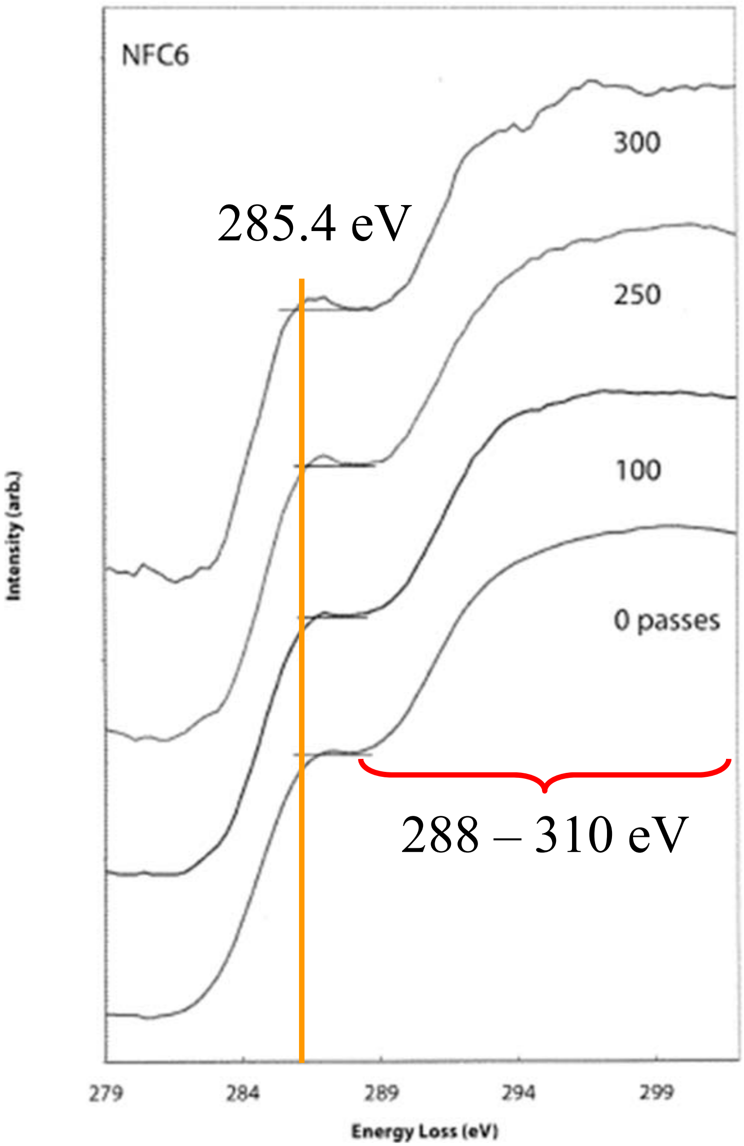
Bright field TEM micrograph of carbon film material (from NFC6) attached to the tungsten tip after sliding.

Results and Discussion

- Reason:
  - ✓ The film debris attached to the tip appears both significantly brighter than the tungsten tip, and
  - ✓ Nearly identical in structure to the standalone NFC film.

- The source of carbon: A combination of material worn from contamination layers built up due to the electron beam as well as worn material from the carbon sample.

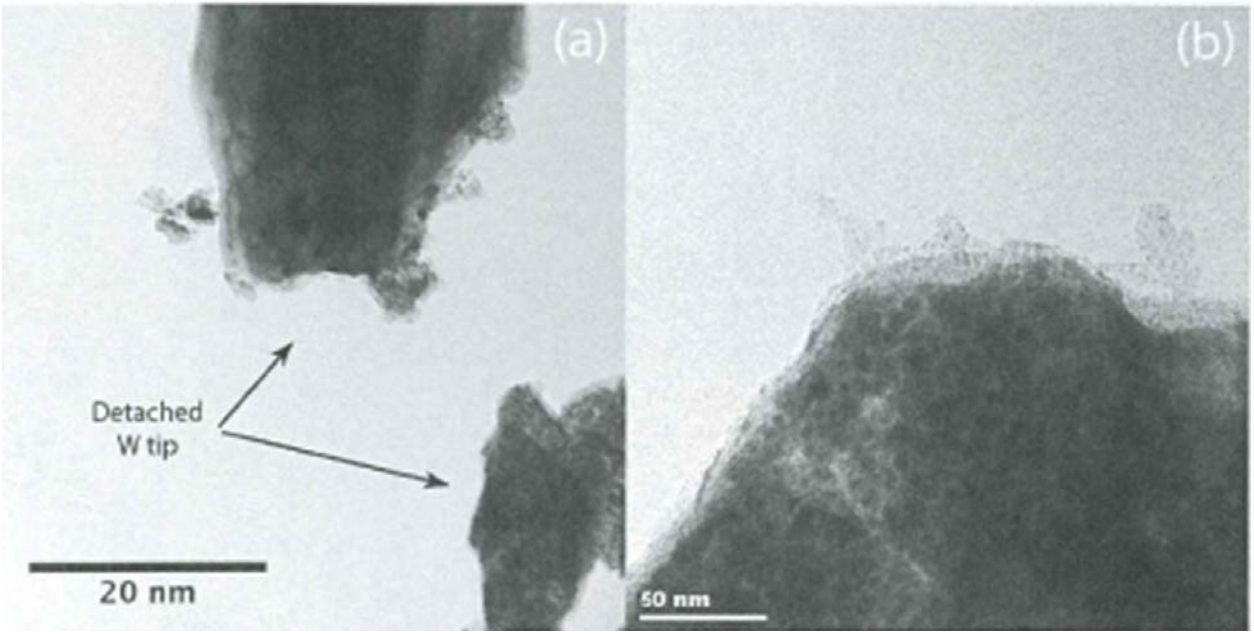
Results and Discussion: NFC6



EELS spectra

- ❖ At 285.4 eV: A pre-edge resonance due to transitions from the C 1s orbital to the unoccupied π^* orbitals originating from sp and sp^2 sites if they are present.
- ❖ 288-310 eV: A broad band is present as a result of overlapping of C 1s $\rightarrow\sigma^*$ transitions at the sp, sp^2, and sp^3 sites of the DLC film.
- ❖ Mechanical excitation induced formation of graphitized carbon.

Results & Discussion: NFC7



❖ No indication of increase in the π* peak after sliding.

❖ More wear debris was produced.

- ❑ The end of the tungsten tip was fractured after only 200 passes.
- ❑ Wear rate (mm^3/N-m): NFC7 – 9 x 10^{-9} and NFC6 – 4.6 x 10^{-10}.
- ❑ Friction coefficient: NFC7 – 0.015 and NFC6 – 0.003 in dry N_2.
- ❑ No evidence of graphitic transfer layer in NFC7.

Conclusions

- EELS showed successive increases in the 1s-πcarbon peak ratio for NFC6, whereas no variations were observed for NFC7.
- Local mechanical excitation result in an increase in local relative sp^2 bonding and graphitization effects.
- Superior lubricity properties of NFC6 as compared to NFC7 are a function of the higher hydrogen content of NFC6 films.

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Questions ??

Thanks !!