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Combined TEM and EELS study of tribologically induced phase transformations of PECVD-grown diamond coatings

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Introduction

Diamond coatings have been demonstrated to be wear-resistant coatings of high quality. Great effort has been put in the study of the mechanism behind. The performance under wear and friction is mainly attributed either to passivation of dangling bonds or to a phase transition from sp^3 to sp^2 at the sliding surfaces [1,2]. In this study, direct evidence of a tribo-induced phase transition between crystalline diamond and amorphous carbon is presented. The characteristics of the amorphous C-layer were studied by electron microscopy combined with electron energy loss spectroscopy.

Electron Microscopic Techniques

- Scanning electron microscopy (SEM)
- Conventional and high-resolution transmission electron microscopy (TEM, HRTEM), scanning transmission electron microscopy (STEM) :
  FEI Titan^3 80-300 with C_s-corrector implemented in the image lens system
- Electron energy loss spectroscopy (EELS) with a Gatan Imaging Energy Filter (GIF) Tridiem model 865 HR:
  micro-probe STEM EELS performed at 80 keV under magic angle conditions [3]
- TEM cross-section sample preparation:
  FIB lamella to select specific areas from inside and outside the wear track
  Conventional preparation to avoid possible artifacts from FIB preparation

Deposition of Diamond Layer and Tribological Testing

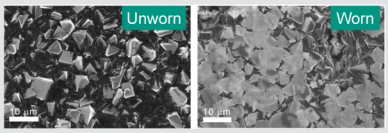
- Plasma-enhanced chemical vapor deposition (PECVD)
- Tribological testing by twin-disc tribometer

Results

SEM

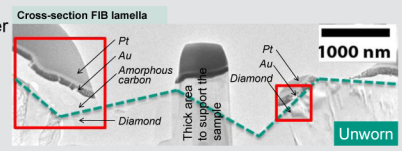
Unworn region:
- Pyramidal grains
- Grain size 4 - 6 µm

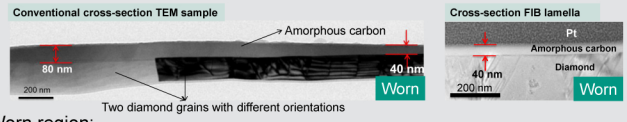
Worn region:
- Flattened surface
- Asperity tips removed
- Height of the removed tips: several µm



TEM

Unworn region:
- Preexisting amorphous C-layer
  - Varying thickness up to several 100 nm
  - Non-homogeneous
  - Non-continuous
  - Porous





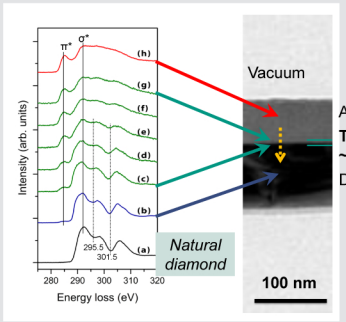
Worn region:
- Tribo-induced amorphous C-layer
  - Rather homogeneous thickness between 40 nm and 80 nm
  - Continuous
  - Without pores

References

[1] L. Pastewka et al., Nature Materials, 10 (2011), 34 – 38.
[2] A. Erdemir et al., Trib. Trans., 40 (1997), 4, 667 – 675.
[3] B. Jouffrey et al., Ultramicroscopy, 102 (2004), 61 – 66.
[4] M. Roy et al., Diamond Relat. Mater., 20 (2011), 573 – 583.
[5] M. I. De Barros et al., J. Phys. Chem. C, 116 (2012), 6966 – 6972.

EELS (inside the wear track)

- Bulk diamond: absence of π* peak; similar σ* features as natural diamond
- Transition region (from bulk diamond to amorphous layer): π* pre-peak increases; smoothening of dips characteristic for diamond
- Amorphous C-layer: pronounced π* peak; featureless σ* peak.

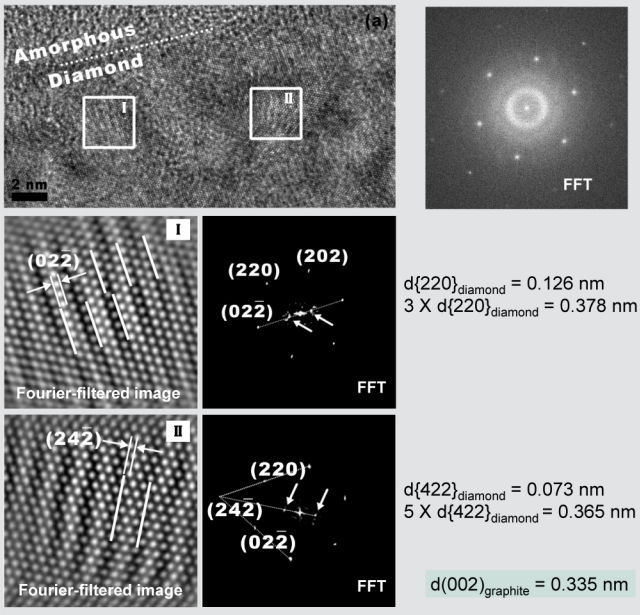


Natural diamond (for reference)
- *Absence of π* peak: pure sp^3-hybridized carbon*
- *Two dips (~295.5 eV and ~301.5 eV): characteristics for diamond structure [4]*

Carbon K-edge of natural diamond particle (a) and line profile crossing the interface (b-h)

HRTEM (inside the wear track)

- Interface region, [111] zone-axis
- Fringes with a distance of 0.36 - 0.37 nm: graphite-like structure
- Two kinds of lattice matching relationships (see below)



$d\{220\}_{diamond}$ = 0.126 nm
3 X $d\{220\}_{diamond}$ = 0.378 nm

$d\{422\}_{diamond}$ = 0.073 nm
5 X $d\{422\}_{diamond}$ = 0.365 nm

$d(002)_{graphite}$ = 0.335 nm

Conclusions & Summary

- The amorphous layer on top of the unworn diamond coating is induced in the last stage of deposition [5] and is removed during tribological testing.
- The amorphous layer on top of the coating in the wear track is tribo-induced.
- The diamond coating bulk contains almost pure sp^3-hybridized carbon.
- In the tribo-induced amorphous layer, the sp^2-fraction is in the order of 70%.
- The transition region between crystalline diamond and amorphous carbon is narrow (~10 nm).
- HRTEM shows graphite-like structures in the transition area. Diamond {220} and {422} planes offer positions for graphite basal planes every 3 and 5 layers.