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Electron microscopic evidence for a tribologically induced phase transformation as the origin of wear in diamond

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Tribological testing of a coarse-grained diamond layer, deposited by plasma-enhanced chemical vapor deposition, was performed on a ring-on-ring tribometer with a diamond counterpart. The origin of the wear of diamond and of the low friction coefficient of 0.15 was studied by analyzing the microstructure of worn and unworn regions by transmission and scanning electron microscopy. In the worn regions, the formation of an amorphous carbon layer with a thickness below 100 nm is observed. Electron energy loss spectroscopy of the C-K ionization edge reveals the transition from sp^3 -hybridized C-atoms in crystalline diamond to a high fraction of sp^2 -hybridized C-atoms in the tribo-induced amorphous C-layer within a transition region of less than 5 nm thickness. The mechanically induced phase transformation from diamond to the amorphous phase is found to be highly anisotropic which is clearly seen at a grain boundary, where the thickness of the amorphous layer above the two differently oriented grains abruptly changes. © 2014 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4865742]

I. INTRODUCTION

Diamond coatings produced by plasma-enhanced chemical vapor deposition (PECVD) have been demonstrated as tribological coatings of high quality.¹⁻³ Despite its high hardness, it was experimentally observed that diamond can exhibit low wear resistance for certain crystallographic orientations of the surface and the polishing directions.^{4–6} The friction behavior of diamond is strongly influenced by the passivation of dangling bonds during sliding in a water-vapor containing atmosphere,^{7,8} which can lead to ultralow friction coefficients below 0.1.9 Another source of low friction was assigned to the formation of a layer containing sp^2 -hybridized C-atoms. The latter was investigated in detail by molecular dynamics simulations by Pastewka et al.¹⁰ who attribute the low wear resistance to the gradual destruction of the diamond surface and the formation of a resulting amorphous interface layer. The transformation from crystalline diamond into the amorphous phase is predicted to be accompanied by a change of bonding configuration from pure sp^3 -hybridization to a substantial fraction of sp^2 - (60%) and sp-hybridized (20%) C-atoms.^{10,11} Indications for such a phase transformation were already experimentally obtained. For instance, Raman spectroscopy provides information about the sp^3/sp^2 -ratio of carbon bonds on a micrometer scale and has been used for phase characterization in diamond films.¹²⁻¹⁵ Nevertheless, clear experimental evidence for this proposed mechanically driven phase transformation of diamond to amorphous carbon as the origin of wear is still lacking.

Previous experimental studies do not allow direct correlations between microstructure and hybridization of C-atoms on the nanometer scale. Efforts have been undertaken to perform combined transmission electron microscopy (TEM) and electron energy loss spectroscopy (EELS) studies to get more insight into the processes which determine the wear resistance. These analytical techniques are the only ones which are suited to resolve the crystal structure and chemical bonding at one and the same position at nanometer resolution. The bonding configuration can often precisely be identified by analyzing the energy-loss near-edge structure (ELNES) of ionization edges, i.e., the C-K ELNES for carbon.¹⁶ An example is the work of Erdemir et al.¹⁷ who investigated debris particles collected from wear tracks formed under different tribological conditions and found sp^2 -hybridized carbon by EELS/ELNES studies in a TEM. However, firm conclusions would require a comparison of tribologically tested samples from worn and unworn regions. Due to the high hardness of diamond and diamond-like carbon, TEM sample preparation is unfortunately very difficult, even though focused-ion-beam (FIB) instruments are now available for the preparation of TEM lamellae from such hard coatings at locations which can be selected with sub-micrometer precision.¹⁸ Using such site-selective FIB preparation and TEM, Tang et al.¹⁹ observed an amorphous carbon (a-C) layer containing sp^2 -coordinated carbon on top of a polished diamond grain after dynamic friction polishing against a metal disk. These results are very instructive but not conclusive regarding the wear of diamond because of the metal counter surface which produces a chemically intermixed tribolayer.

In this work, the microstructural properties and chemicalbonding changes caused by tribological testing are presented for pure diamond. Diamond films were deposited on silicon carbide (SiC) substrates and tested against the same kind of diamond films. Analytical results were obtained by conventional TEM and high-resolution TEM (HRTEM) in combination with quantitative EELS/ELNES. An a-C layer was clearly detected after tribological testing. The bonding characteristics in this tribolayer change within less than 5 nm from pure sp^3 -hybridization in crystalline diamond to a substantial fraction (65%) of sp^2 -hybridized C-atoms in the tribo-induced a-C layer.

II. EXPERIMENTAL TECHNIQUES

Diamond films were deposited by microwave plasmaenhanced chemical vapor deposition. The substrates were first seeded by ultrasonic attenuation in ethanol with diamond powder (0–300 nm). The diamond film was grown in a gas atmosphere containing 1.7% CH₄ and 98.3% H₂ on a SiC-substrate heated to 900 °C. The hardness and Young's modulus of the resultant film were measured to be 9425 (\pm 5%) HV and 762 (\pm 2%) GPa, respectively. Ring-on-ring tribological tests at a relative speed of 4 m/s were performed in a nitrogen atmosphere under a global pressure of ~2 MPa. Both counterparts were coated with the same kind of diamond layer. The wear rate was 0.6 μ m/h. Wear was confined to the polishing of the grain asperities. A wear track of 2 mm width with a shiny appearance was formed on the diamond surface. A friction coefficient of 0.15 was measured by the end of the test.

Before preparation of TEM samples, the surface topography of the diamond film was imaged by scanning electron microscopy (SEM) with secondary electrons in a LEO Gemini 1530 microscope operated at 10 kV. FIB milling with 30 keV Ga⁺-ions was then applied to prepare cross-section samples from unworn regions of the diamond film as well as from the wear track. An approximately 100 nm thick gold layer was deposited on top of the diamond film before milling to mark the original surface of the diamond layer. A Pt/C-layer was additionally deposited for sample protection prior to FIB milling. Thinning was performed to a thickness of \sim 50 nm by applying 5 keV Ga⁺-ions for the final thinning step to minimize damage by the Ga⁺-ions. For comparison, cross-section TEM samples were prepared in the conventional way, i.e., by sawing, grinding, polishing, and subsequent 2.5 keV Ar⁺-ion thinning, to check for possible artifacts of the FIB-lamella preparation.

TEM and HRTEM imaging was carried out at 300 keV in an FEI Titan³ 80–300 microscope. The microscope is equipped with a hexapole corrector for spherical and other aberrations in the imaging lens system which yields HRTEM images with an information limit of 0.08 nm. EELS analyses were performed in the Titan microscope using a Gatan imaging energy filter (GIF, Tridiem 865 HR). The energy dispersion was set to 0.1 eV/channel. To minimize electron-beam damage during EELS analyses, the microscope was operated in the microprobe STEM mode at 80 keV. The full width at half maximum (FWHM) electron-beam diameter in this mode is 2.7 nm. The energy resolution measured by the FWHM of the zero-loss beam amounts to approximately 0.6 eV. EELS spectra were taken along lines of defined lengths by control of the electron probe through the microscope software TIA (TEM Imaging and Analysis, FEI).

The fraction of sp^2 -hybridized C-atoms was determined by exploiting the ELNES of the C-K ionization edge.^{20–22} For this purpose, reference EELS spectra of the C-K edge of highly oriented pyrolytic graphite (HOPG) and natural diamond were acquired using the same acquisition parameters (80 keV primary electron energy, 2.0 mrad beam convergence semi-angle, and 8.3 mrad spectrometer acceptance semi-angle) as for the analysis of the tribologically tested diamond layer. Beam convergence angle and spectrometer acceptance angle were chosen to comply with so-called "magic-angle" conditions,^{23,24} which yield EELS spectra independent of the incidence direction of the electron beam with respect to the graphite lattice. The fraction of sp^2 -hybridized C-atoms in this work was quantified by measuring the ratio of π^*/σ^* -intensities similar to the procedure suggested by Berger et al.²⁰ Processing of the EELS spectra was performed with the DigitalMicrograph software (Gatan Inc.). The background signal was subtracted by fitting the pre-edge region with a power-law function and extrapolating it to the edge region. Multiple scattering was removed by Fourier deconvolution with the low-loss spectrum. The energy windows for integrating the intensities under π^* and σ^* excitations were chosen from 285 eV to 285.4 eV and from 291 eV to 301 eV, respectively.

III. EXPERIMENTAL RESULTS AND DISCUSSION

The SEM images in Fig. 1 obtained from outside (Fig. 1(a)) and within the wear track (Fig. 1(b)) allow a comparison of the surface topography of the diamond films as-prepared and after tribological testing. The pristine surface of the diamond layer is characterized by a rough



FIG. 1. SEM images from (a) the pristine diamond layer and (b) the wear track.

topography with grains, which often exhibit pyramidal shapes and typical grain sizes in the μ m-range. Cross-section SEM images (not shown here) yield the thickness of the diamond film which varies between 4 μ m and 7 μ m due to its coarse-grained structure. The surface was flattened after tribological testing (Fig. 1(b)). A significant amount of material was obviously removed. Cross-section SEM yields a remaining film thickness of ~4.5 μ m in the wear track.

Cross-section TEM images of the as-prepared diamond film are presented in Fig. 2. Fig. 2(a) shows an overview image of the lamella. For mechanical stabilization, the FIB lamella contains a bar with larger thickness in the center of Fig. 2(a). Material was inhomogeneously removed by the Ga⁺-ion milling which can be inferred from the partial lack



FIG. 2. Cross-section TEM images of the as-prepared diamond film. (a) overview of the FIB lamella with the original surface of the coating marked by a dashed line; (b) enlarged TEM image of the region marked by (1) in (a); (c) DF TEM image of the region marked by (2) in (a). The DF TEM image was taken with a $\{2\bar{2}0\}$ reflection as indicated by the [111] zone-axis pattern obtained by selected-area electron diffraction. The surface of the diamond layer is marked by a white dashed line.

of the Au- and Pt/C-cover layers, which are still present in the regions marked by frames. Nevertheless, the original surface of the as-prepared diamond can be well traced and is indicated by the dashed line. It confirms the rough surface topography showing grains with pyramidal shape and sizes in the μ m-range. The height of the pyramids may be actually larger because the cross-section was not necessarily taken through the center of the grains. Fig. 2(b) shows the region marked by frame (1) in more detail. The layer with the darkest contrast and a thickness of 100 nm is the gold layer, which marks the original surface of the as-prepared diamond film. The Pt/C-layer protection layer on top of the Au-layer exhibits a brighter contrast. The lower part of the image shows crystalline diamond. In addition, an a-C layer with a thickness of up to \sim 500 nm is observed between the Au-layer and the crystalline diamond. The a-C contains pores with a size of up to 300 nm which are attributed to inhomogeneous FIB milling in this thin sample region. Fig. 2(c) shows a dark-field (DF) TEM image taken with a $\{2\overline{2}0\}$ reflection from the region marked by frame (2) in Fig. 2(a). Here, the a-C layer is missing as demonstrated by stacking faults reaching up to the nanocrystalline Au-layer (white arrow in Fig. 2(c)) which delineates the original surface of the diamond film (marked by a dashed line). The crystallinity of the diamond layer is confirmed by selected-area electron diffraction (SAED) (see SAED pattern in [111] zone-axis inset in Fig. 2(c)). It can be concluded from Figs. 2(b) and 2(c) that the as-deposited diamond layer is covered by a porous a-C layer with an inhomogeneous thickness. The layer can locally be absent (Fig. 2(c)) or may be up to \sim 500 nm thick as seen in Fig. 2(b).

Fig. 3 shows cross-section TEM images of the tribologically tested region. A TEM image of the lamella prepared by FIB milling is presented in Fig. 3(a). The image shows the crystalline diamond film, an a-C layer with a thickness of 30 to 50 nm and the Au-protection film with its darker contrast on top. The surface of the diamond film is rather flat as expected from the SEM image Fig. 1(b). To check for possible amorphization of the near-surface region of the crystalline diamond due to FIB preparation, a TEM sample from the wear track could be successfully prepared by conventional techniques. The TEM image Fig. 3(b) confirms the findings of the FIB-prepared sample. It shows a well adhering continuous a-C layer with a thickness between 40 nm and 80 nm on top of the crystalline diamond layer. We note that the lower part of the diamond layer was removed during Ar⁺-ion milling. The effect of the amorphization by the Ar⁺-ion milling can be well assessed at the lower edge of the TEM sample marked by the black arrow. Only a narrow amorphous region with $\sim 15 \text{ nm}$ width can be recognized. The thin a-C layer induced by Ar⁺-ion clearly demonstrates that the a-C layer on top of the diamond layer is not an artifact of the FIB sample preparation.

Two grains with different contrast are visible in Fig. 3(b). The grain with dark contrast is oriented close to a zone-axis orientation. Kinematic diffraction conditions without the effect of strong Bragg diffraction yield bright contrast in the other grain indicating a significant orientation difference between the two grains. Close inspection of the



FIG. 3. Cross-section TEM images taken from the wear-track region. (a) Overview TEM image of a FIB lamella; (b) Overview TEM image of a conventionally prepared TEM sample; (c) HRTEM image of the interface region between crystalline diamond and the tribo-induced amorphous carbon layer with the diamond oriented along the [111] zone axis. The approximate position of the interface is marked by a dashed line. The inset shows a crystalline diamond nanoparticle embedded in the a-C layer.

interface between the two grains (white arrow in Fig. 3(b)) reveals a step with a height of $\sim 10 \text{ nm}$ which effectively changes the thickness of the a-C layer on top. Fig. 3(c) shows a HRTEM image of the interface region between diamond and the a-C layer taken from the FIB-prepared sample. The diamond is oriented along the [111] zone-axis. Fig. 3(c)shows that the interface (indicated by a dotted line) is not atomically flat but exhibits a small-scale peak-to-peak roughness of \sim 1 nm on a lateral scale of a few nm along the interface. On the lateral scale of typical TEM specimen thicknesses of several 10 nm, the roughness is in the same order (1-2 nm). The interface in Fig. 3(c) is oriented almost parallel to a {121} lattice plane. HRTEM images of the a-C layer occasionally reveal crystalline diamond nanoparticles with sizes below 5 nm (inset in Fig. 3(c)), which are embedded in the tribo-induced a-C layer.

The a-C layers observed on as-deposited and on tribologically tested diamond differ significantly as far as thickness and morphology are concerned. The a-C layer with a thickness of up to several 100 nm on as-deposited diamond is attributed to the plasma deposition process. According to De Barros et al.,⁹ an a-C layer can indeed be present on the pristine diamond film as deposit from remnant precursor gas after the termination of the active PECVD process. For the tribologically tested region of the film, the SEM image Fig. 1(b) and TEM images (Fig. 3) demonstrate that the μ msized grains at the rough original diamond surface are almost completely flattened indicating that a significant amount of material must have been removed including the residual a-C layer from the deposition process. In contrast to the asdeposited a-C residue, the tribo-induced a-C layer is comparably uniform with a thickness below 100 nm. The large size of the grains and comparably small electron-transparent region of the TEM samples did not allow a statistically significant determination of the crystallographic orientation of the interface between the a-C layer and crystalline diamond. However, in the few cases, where this analysis was possible, we observe interface orientations close to $\{112\}$ or $\{110\}$ planes (not shown).

A few of the TEM-samples containing a tribo-induced a-C layer contain grain boundaries of the underlying polycrystalline diamond in the electron transparent region. It is found that the thickness of the a-C layer changes quite abruptly on grains with different crystallographic orientations (cf. Fig. 3(b)). Fig. 3(c) clearly shows that the interface between the crystalline diamond and the tribo-induced amorphous a-C layer is not crystallographically flat but displays a nm-scale roughness.

Taking these observations together, we can identify characteristics of the wear process of diamond. First, the wear process clearly involves the generation of a triboinduced amorphous carbon layer. This carbon layer is softer than diamond and therefore lubricates the contact which in turn correlates well with the rather low friction coefficient of diamond. The actual wear rate is then determined by two processes, the removal of the amorphous carbon layer and, of course, the growth rate of the amorphous carbon layer into the diamond. The removal of the amorphous carbon may proceed mechanically by plowing in front of diamond asperities,¹⁰ which results in the formation of wear debris, or by chemical etching with ambient oxygen.^{11,25,26} The most essential process, however, is the growth of the amorphous phase into the crystalline diamond which must be interpreted as a mechanically driven phase transformation. The nmscale roughness of the crystal-amorphous interface could also be compatible with the removal of small clusters from the crystal but most likely indicates an atom-by-atom amorphization process. Such an atomistic process in which the shearing of the softer amorphous phase over the interface occasionally removes an atom from the crystal is what is also observed in atomistic simulations.^{10,27}

Another very strong indication of such atom-by-atom phase transformation process is the different height of the amorphous layers above differently oriented grains as seen in Fig. 3(b). This observation directly suggests that the two crystals underneath the shearing amorphous layer must give in to the amorphization process with different ease. It indicates a very strong crystallographic anisotropy of the rate of amorphization of the crystal at the interface. That wear rate of diamond is anisotropic and depends on the crystallographic orientation has been known for some time by means of polishing single crystalline diamonds in specific orientations^{4–6} and has also been found in atomistic simulation.¹⁰ Tribological experiments with $\langle 100 \rangle$ and $\langle 111 \rangle$ fiber-textured diamond films show that the wear rate and coefficient of friction differ for particular crystal planes with overall polishing orientations.²⁶ All the previous observations clearly demonstrate a crystallographic anisotropy of wear in diamond but have to remain unspecific about the origin of this anisotropy. Our observation now directly demonstrates that it is the growth rate of the amorphous-crystalline interface which is different for different crystallographic directions.

Diamond nanoparticles embedded in the a-C layer, which are also found in the amorphous layer, could come from an occasional breaking-off of diamond nanocrystals from the interface. However, this is regarded as rather unlikely given the different indications for an atom-by-atom transformation process. The diamond nanocrystals could also be remainders of larger fractured diamond pieces or they could be generated from within the amorphous phase in the tribological experiment. Although we cannot clarify precisely the origin of the nanocrystals it is worth noting that such diamond nanoparticles were also observed by van Bouwelen *et al.*²⁸ in the debris produced by polishing diamond.

We next focus on the structure of the tribo-induced amorphous layer. Fig. 4 presents results of a combined TEM and EELS/ELNES analysis of the microstructure and bonding configuration of the C-atoms close to the interface between crystalline diamond and the tribo-induced a-C layer.



FIG. 4. (a) Cross-section TEM image of the transition region between crystalline diamond and the a-C layer with the direction of the EELS line-profile indicated. (b) EELS spectra of the C-K edge for (1) natural diamond, (2)–(8) line-profile EELS spectra across the interface between bulk diamond and the tribo-induced a-C layer, (9) reference spectrum recorded from HOPG.

Fig. 4(a) shows a cross-section TEM image with dots indicating the position of EELS line-profile analysis across the diamond/a-C interface with the corresponding EELS spectra of the C-K ionization edge in Fig. 4(b). Spectrum (2) in Fig. 4(b) was taken in the bulk crystalline diamond. This spectrum can be compared with a reference spectrum (1) acquired from natural diamond which contain 100% sp^3 -hybridized C-atoms. Spectra (1) and (2) show the well-known ELNES signature of sp^3 -hybridized C-atoms which consists of a peak at an energy loss ΔE of ~292 eV associated with σ^* states and two dips at \sim 295.5 eV and \sim 301.5 eV.²² We note a low-intensity pre-peak at $\Delta E = 285 \text{ eV}$, which can be assigned to a small fraction of sp^2 -hybridized C-atoms. This is deduced from a reference spectrum taken from 100% sp²-hybridized HOPG (spectrum (9) in Fig. 4(b)), which shows a pronounced pre-peak at $\Delta E = 285 \text{ eV}$ resulting from π^* states. The small π^* pre-peak in spectrum (2) is attributed to the disordered surface layer superimposed on crystalline diamond due to TEM sample preparation.

Spectra (2) to (8) in Fig. 4(b) were taken in $\sim 2 \text{ nm steps}$ across a 10 nm interval between crystalline diamond and the a-C layer. A continuous rise of the π^* pre-peak is observed which is characteristic for an increasing fraction of sp^2 -hybridized C-atoms. Smoothing of the dips is another well-known feature of a-C.^{20,21} Considering the effects of the 2.7 nm probe diameter, 1-2 nm interface roughness and possible slight inclination of the electron beam with respect to the interface, the true width of the transition layer in which the π^* peak rises to its bulk value is likely to be below 5 nm. Spectrum (8) was taken in the a-C layer outside of the transition region. The pronounced π^* peak indicates a high fraction of sp^2 -hybridized C-atoms. The σ^* peak is broadened and featureless due to the amorphous structure. The evaluation of the ratio of the π^*/σ^* -intensities with respect to the reference spectrum (9) yields a fraction of $\sim 65\%$ sp^2 -hybridized C-atoms. We note a more rounded onset of the σ^* peak in spectrum (2) compared to the reference spectrum (1). The loss intensity between 287 eV and 290 eV could be assigned to the σ^* state of C-H bonds. Intensity in this energy loss range was shown to correspond to C-H bonds or tetrahedral amorphous carbon in a study by X-ray absorption near-edge structure spectroscopy.²⁹ The latter origin can be excluded in crystalline diamond whereas hydrogen is indeed expected in diamond deposited by PECVD.³⁰ The rounded onset of the σ^* peak gradually decreases in spectra (3) to (6) and approaches the shape of the reference HOPG spectrum (9). This shows the reduction of the H-content in the tribo-induced C-layer, indicating a loss of hydrogen to the environment through free surfaces.

The bonding characteristics in the tribo-induced amorphous carbon layer is dominated by a content of 65% sp^2 -hybridized C-atoms according to our quantitative EELS results. With the high content of sp^2 -hybridized C-atoms, it is plausible that the a-C acts as a lubricant layer and is responsible for the low friction coefficient of diamond. The amount of 65% sp^2 -hybridized C-atoms found here agrees well with the 60% sp^2 -hybridized C-atoms obtained in tribosimulations¹⁰. However, a gradual transition of the sp^2 -content as found here has never been observed before

and is also not seen in simulations. Its origin must therefore be investigated further.

Erdemir et al.¹⁷ carried out tribological tests on a smooth diamond surface sliding against a Si₃N₄ ball in a dry N₂-atmosphere, where the friction coefficient decreased from an initially high value of 0.6 to 0.04. This behavior was attributed to the transformation of debris particles into graphitic carbon. Erratic increase of the friction coefficient to high values was proposed to be caused by the removal of graphitic debris from the sliding interface. A similar mechanism was proposed by Hird et al.¹⁵ Tang et al.¹⁹ also observed a thin graphitic a-C layer on top of crystalline diamond after dynamic friction polishing against a metal wheel. They attributed the phase transformation from diamond into amorphous carbon to high temperatures above 1000 °C during polishing combined with possible catalytic activity of transition metal impurities observed in the debris layer. In the present study, experimental conditions are such that even locally high temperatures above 1000 °C are very unlikely and catalytic metallic components are not involved in the tribocontact. Consequently none of these can be responsible for the formation of the a-C layer.

The surrounding gas phase also plays an important role in the friction behavior of carbon.⁹ For example, water vapor, H_2 , or other H-/OH-containing molecules in the ambient atmosphere can significantly reduce friction by passivation of the dangling bonds at the diamond surface.⁹ Tribological testing in our study was performed in a N₂-atmosphere, but a trace of O₂ or H₂O vapor cannot be completely excluded. Similarly, a small amount of hydrogen is expected to be released from the PECVD grown diamond as it amorphizes.

While now the mechanically induced phase transformation of diamond to amorphous carbon is clearly identified as the origin of wear and is tentatively linked with the low friction coefficient, it remains elusive how the rate of transformation may depend on experimental conditions and on environment or trace amounts of catalytic components. Further studies will have to investigate these rate effects more carefully and to which extent such phase transformations are a general phenomenon of solid lubrication.

IV. SUMMARY

The microstructure of a polycrystalline PECVD-deposited diamond film was investigated before and after tribological testing against an identical film to analyze the origin of wear of diamond. The formation of an amorphous tribo-induced carbon layer with a rather homogenous thickness below 100 nm is clearly identified as the central mechanism of wear. The amorphous layer is formed by a mechanically induced phase transformation occurring at the interface between the diamond and the amorphous carbon layer. An interface roughness of ~ 1 nm indicates a crystalline-amorphous phase transformation that is induced by an atom-by-atom process. The abrupt thickness change of the amorphous carbon layer on top of grains with different crystallographic orientations demonstrates that the phase transformation process is highly anisotropic.

The tribo-induced amorphous carbon layer is found to contain a high fraction of $65\% sp^2$ -hybridized C-atoms. The

increase of the fraction of sp^2 -hybridized C-atoms occurs within a transition region of less than 5 nm thickness. Although the tribo-induced amorphous carbon layer clearly is at the origin of wear in diamond, its general role as a solid lubricant for the measured friction coefficient remains elusive.

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