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Supplementary Material

Nano-scale coating wear measurement by introducing Raman-sensing underlayer

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S1. Experimental Section

S1.1. Film deposition procedure

The substrates were ultrasonically cleaned by acetone and ethanol. Before the deposition, the vacuum chamber was pumped down to a base pressure of 3.0×10^{-3} Pa and heated to 200 ℃. After that, the substrate surface was etched in argon plasma at the pressure of 0.15 Pa for 5 mins. During the deposition, a pulsed DC bias voltage of -500 V was applied to the substrates and the acetylene pressure was 0.85 Pa.

S1.2. Gaussian peak fitting

EELS spectra of C-K core-edge were collected point by point across the specimens. Gaussian peak fitting was adopted to quantify the bonding fractions within the energy window of 280-310 eV through the Gatan DigitalMicrograph software. To reduce the complexity and instability during fitting, two Gaussian peaks are fitted to π* (C=C) and σ* (C-H) bonds and the residual bond fraction is then assigned to σ* (C-C). To calculate the sp^2 bond (C=C) fraction in the C-K edge, the integrated area of π* peak centered at ~ 285.5 eV is normalized to the total area (π* + σ*) integrated in the window of 280-310 eV and the ratio is then referenced to the standard value (~ 0.119) of highly oriented pyrolytic graphite (HOPG, 100% sp^2-C bonds), according to the following equation [18,19]:

$$sp^2\% = \frac{A_s\,(\pi*)/A_s(total)}{A_{HOPG}\,(\pi*)/A_{HOPG}(total)}$$

where A_s (π*) and A_{HOPG} (π*) are the areas of π* peaks of the samples and HOPG, while A_s (total) and A_{HOPG} (total) are the areas integrated in the energy region of 280-310 eV. The bond fraction of σ^* (C-H) at ~ 287 eV are also obtained by this method.

S2. Results and discussion

S2.1. TEM characterization for obtaining coating thickness

Figure S8a shows the SEM image of lamellar specimen (FIB) in the center area marked in Figure S7. Figure S8b,c display the corresponding TEM images and the actual coating

thickness values were measured at intervals of 300 nm along the horizontal direction. Furthermore, same process was employed to characterize the coating thickness in the side and unworn areas as shown in Figure S9 and S10.

Table S1. Optical parameters of samples with a-C:H coatings of different thickness deposited on glass plates.

Thickness(nm)	T_o (%)	T_1 (%)	T_2 (%)	R_o (%)	R_1 (%)	R_2 (%)	α_o (cm^{-1})	α_1 (cm^{-1})	α_2 (cm^{-1})
15.3±1.6	53.88	54.57	56.27	21.34	21.45	21.52	9.04×10^4	8.01×10^4	5.89×10^4
37.6±2.7	42.04	42.84	44.66	23.24	23.81	24.74	8.97×10^4	8.07×10^4	6.32×10^4
110.4±2.4	24.61	25.83	28.65	19.87	19.71	19.33	8.68×10^4	8.28×10^4	7.43×10^4
183.3±3.0	12.38	13.56	16.4	21.55	21.82	22.66	8.75×10^4	8.21×10^4	7.05×10^4
277.1±2.3	5.20	5.94	7.54	22.03	22.36	23.07	8.87×10^4	8.36×10^4	7.43×10^4

T_o, R_o, and α_o for 488nm light; T_1, R_1, and α_1 for 500nm light; T_2, R_2, and α_2 for 528nm light. The thickness is measured by non-contact optical profilometer.

Table S2. Thickness of as-grown a-C:H coatings measured by different methods.

Thickness (nm) Profilometer	Thickness (nm) Raman Si signal	Thickness (nm) Raman C signal
15.3±1.6	8	16
37.6±2.7	24	71
110.4±2.4	99	109
183.3±3.0	188	147
277.1±2.3	267	283

Table S3. Average values of EELS C-bonds fractions of three targeted areas.

Bond	Unworn area	Side area	Center area
sp^2 (C=C)	59 %	60 %	63 %
sp^3 (C-H)	21 %	18 %	17 %
sp^3 (C-C)	20 %	22 %	20 %

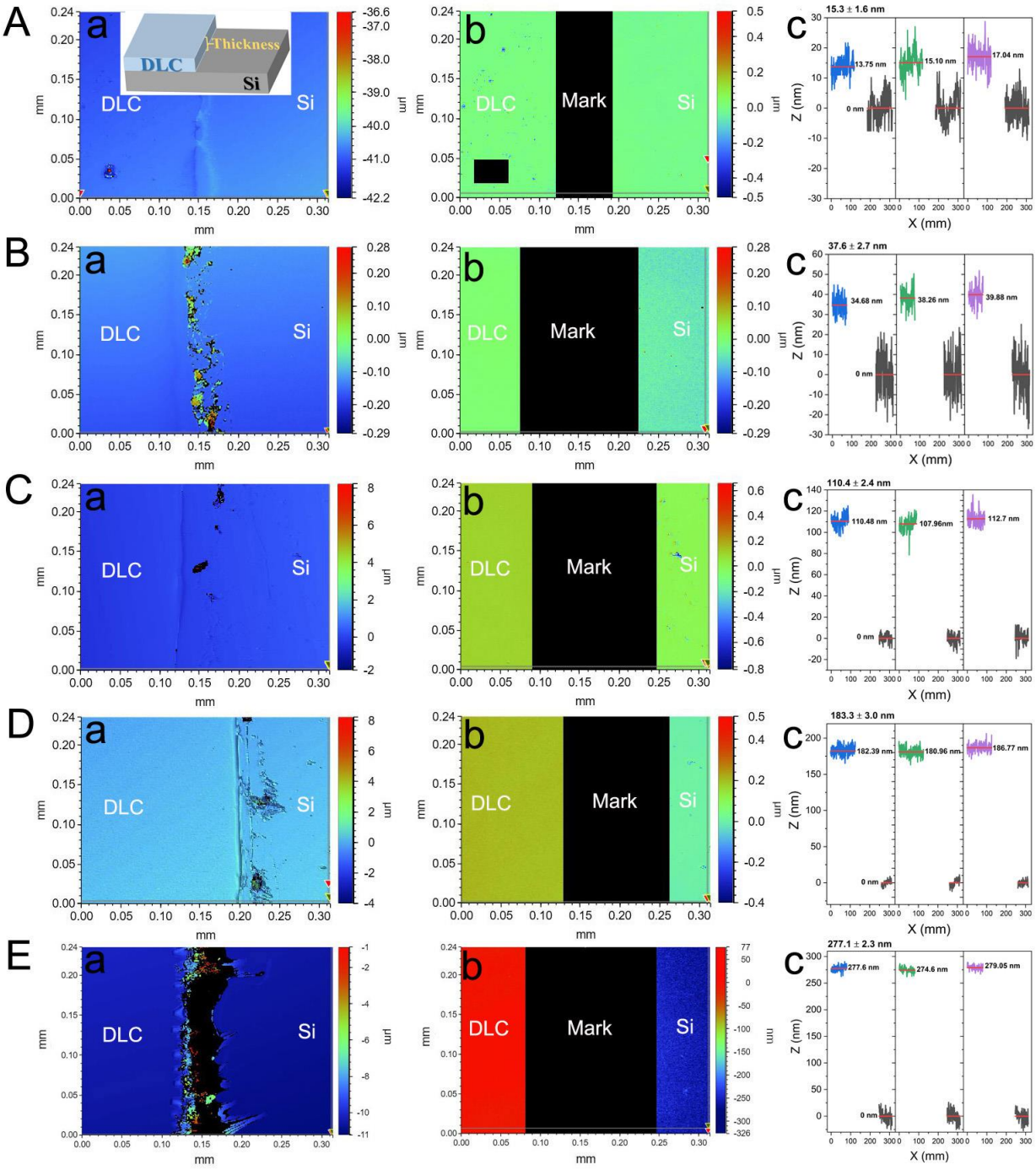

Figure S1. 3D optical microscopy images of samples with a-C:H coatings of different thickness deposited on Si wafers (A, 15.3 nm; B, 37.6 nm; C, 110.4 nm; D 183.3 nm; E, 277.1 nm) and the corresponding step height values (c).

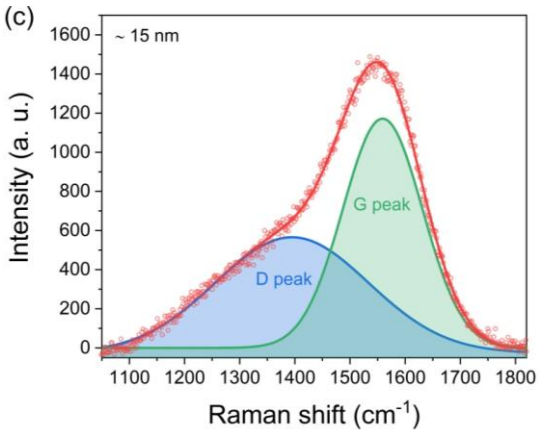

Figure S2. Fitting curves of carbon band by two Gaussians.

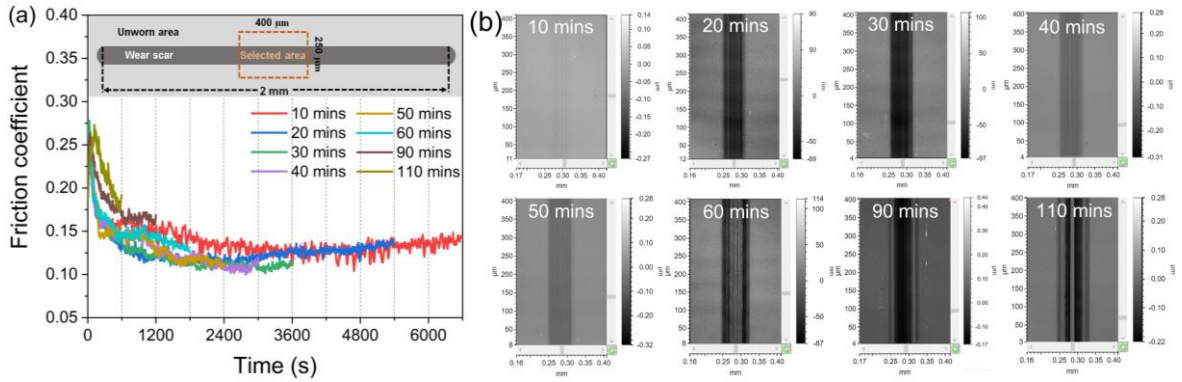

Figure S3. Friction curves of a-C:H film deposited on silicon wafer under different test time in the dry friction (a) and 3D optical microscopic images of the middle areas of wear scars (b).

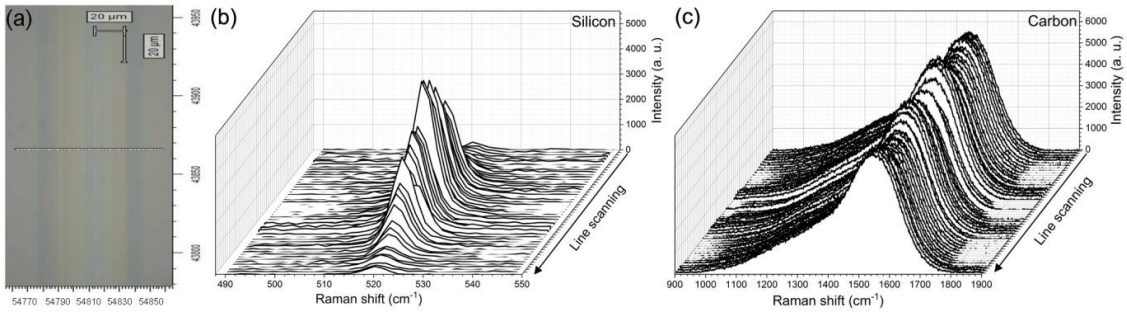

Figure S4. Detailed information of data processing based on Raman spectra of silicon and carbon bands. (a) Optical image of line-scanning trace of Raman spectroscopy across the wear track (tribo-test time: 90 mins). (b) Raman spectra of a series of silicon bands obtained from line-scanning. (c) Raman spectra of a series of carbon bands obtained from line-scanning.

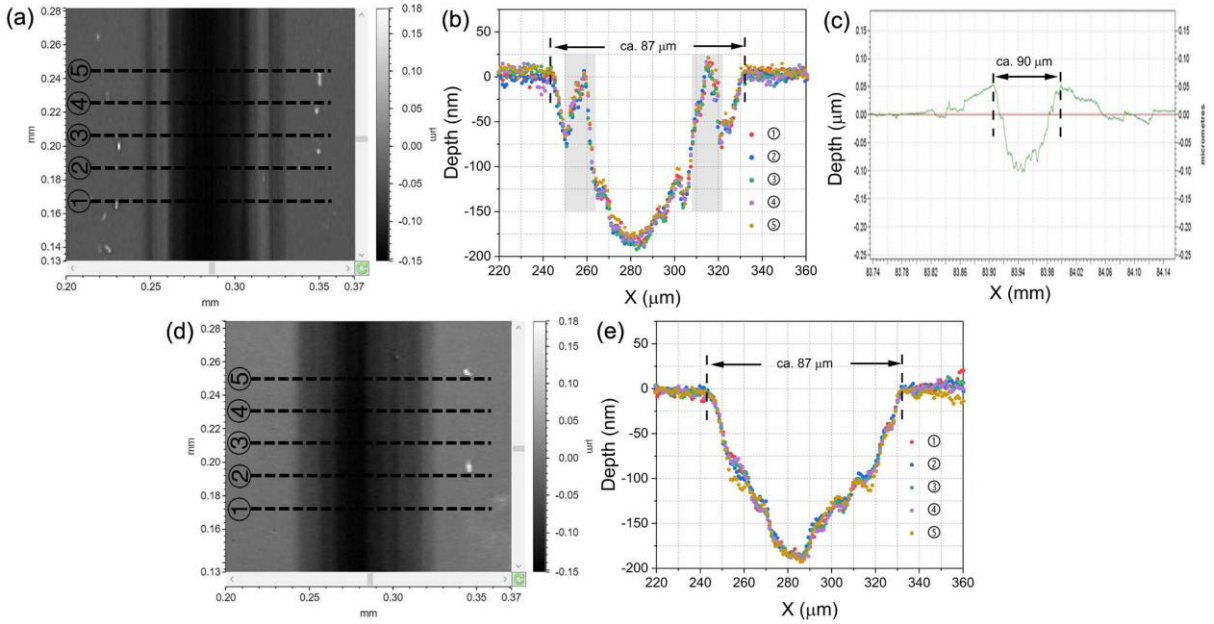

Figure S5. (a) 3D optical image of wear scar after 90 mins tribo-test. (b) Wear profile curves of marked lines in (a) obtained by non-contact optical profilometer. (c) Wear profile curve obtained by contact profilometer. (d) 3D optical image of wear scar of the same sample in (a) with iridium layer deposited on top. (e) Wear profile curves of marked lines in (d) obtained by non-contact optical profilometer.

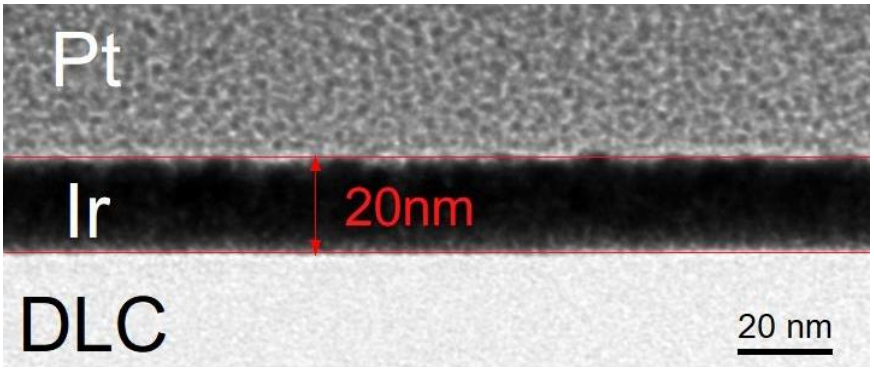

Figure S6. HRTEM image of cross-sectional morphology of the a-C:H surface with iridium and platinum layers. The thickness of iridium is ca. 20 nm which is employed to provide a top surface with consistent optical properties.

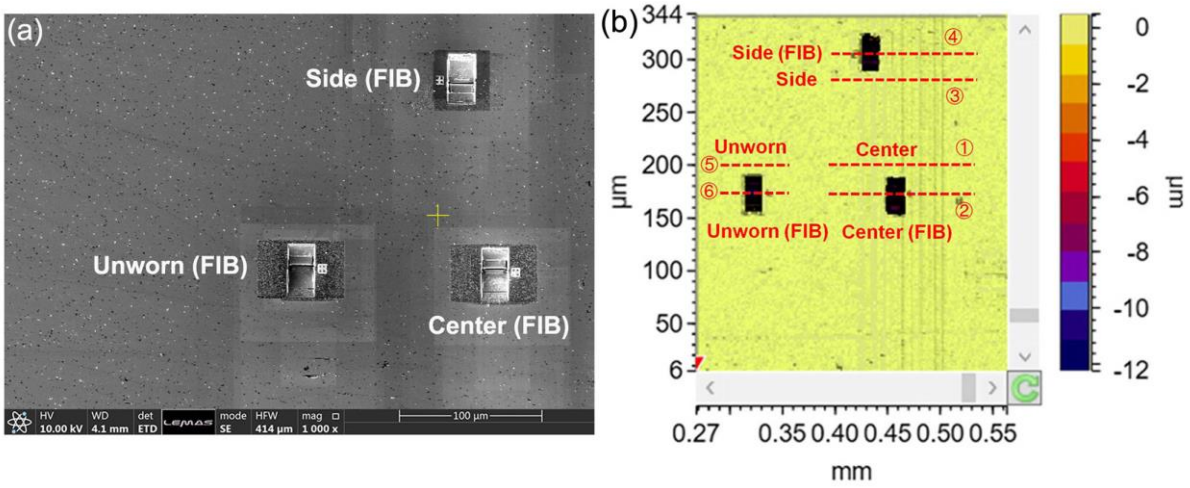

Figure S7. SEM image of wear scar after 90 mins tribo-test (a) and the corresponding 3D optical image obtained by optical profilometer (b). Three typical positions (center, side and unworn areas of wear scar) were selected to provide FIB samples. Non-contact optical profilometer was used to locate actual FIB positions and give wear profile curves across and beside the FIB areas.

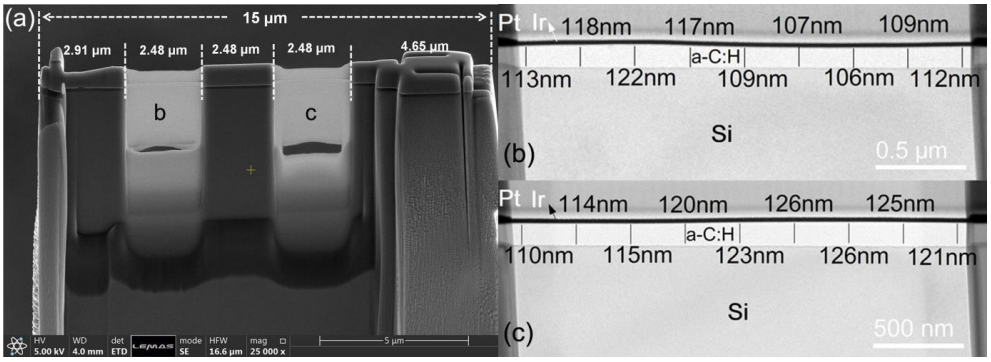

Figure S8. SEM image (a) of cross-sectional morphology of center area in the Figure 5 and the corresponding TEM images ((b) and (c)) in the marked areas as shown in (a).

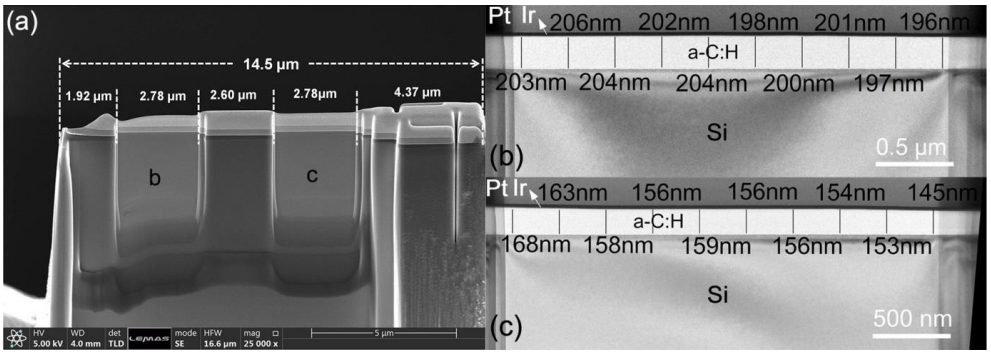

Figure S9. SEM image (a) of cross-sectional morphology of side area in the Figure 5 and the corresponding TEM images ((b) and (c)) in the marked areas as shown in (a).

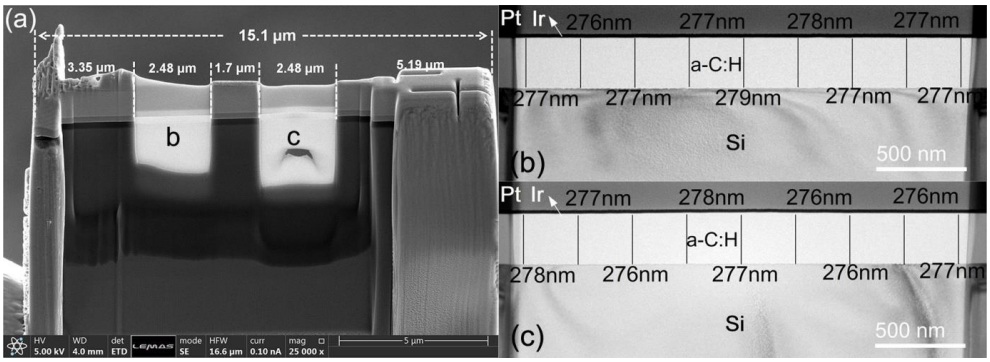

Figure S10. SEM image (a) of cross-sectional morphology of unworn area in the Figure 5 and the corresponding TEM images ((b) and (c)) in the marked areas as shown in (a).

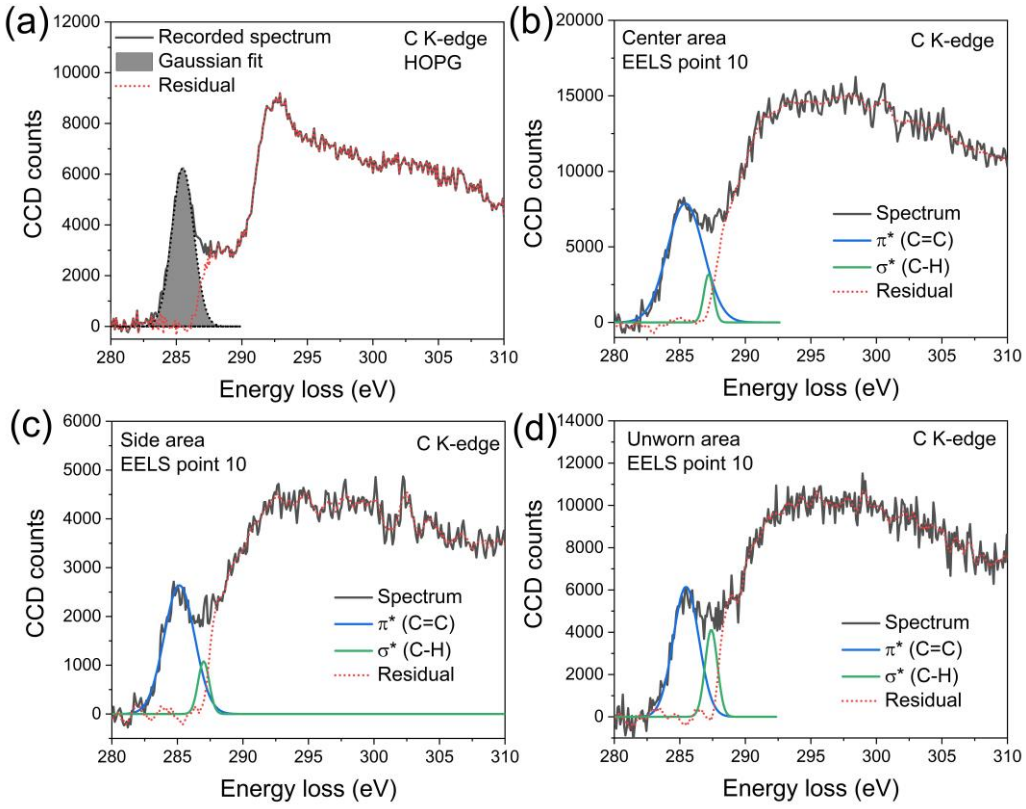

Figure S11. (a) C K-edge spectrum of HOPG in the energy window of 280-310 eV showing a Gaussian fit to the π* peak after background subtraction and deconvolution of the C K-edge spectrum. By normalizing the π* peak area to the integrated area in the energy window of 280-310 eV, a standard value of 0.119 is obtained. (b-d) Examples of peak fitting to the C *K*-edges from center, side and unworn areas. Two Gaussian peaks are fitted to π* (C=C) and σ*(C-H) bonds, respectively. The residual bond fraction is then assigned to σ*(C-C)

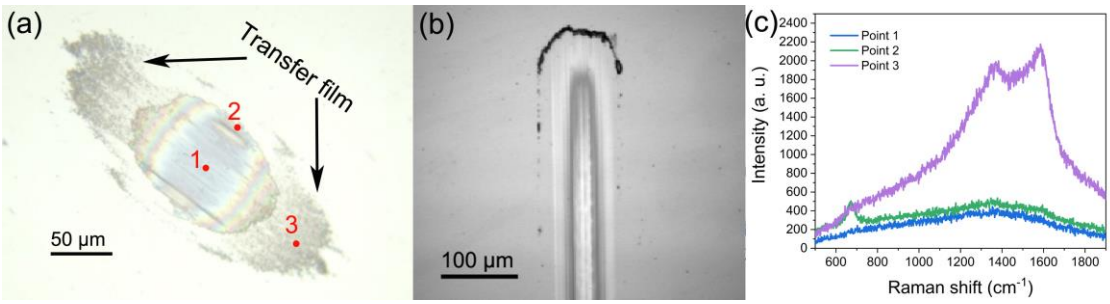

Figure S12. Optical images of wear scars on the steel counterpart ball (a) and a-C:H coating (b), and Raman spectra (c) on the marked points in (a).

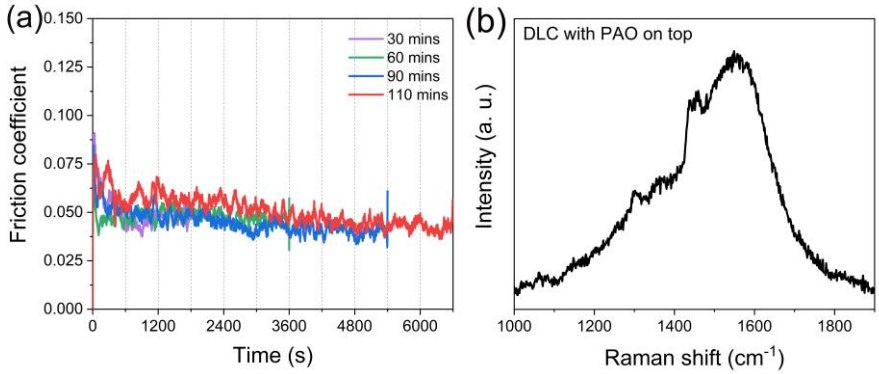

Figure S13. (a) Friction curves of samples with a-C:H deposited on silicon wafer under different test time under oil-lubricated condition (PAO; test time 30-110 mins). (b) Raman spectra of carbon band with oil film on the top (PAO; test time 110 mins).