Supporting information

Probing the tribochemical impact on wear rate dynamics of hydrogenated amorphous carbon via Raman-based profilometry

Nan Xu,[*,†] Chun Wang, [†] Liuquan Yang,[†] Gin Jose,[‡] and Ardian Morina [*,†]

[†] Institute of Functional Surfaces, School of Mechanical Engineering, University of Leeds, Leeds LS2 9JT, United Kingdom

[‡] School of Chemical and Process Engineering, University of Leeds, Leeds LS2 9JT, United Kingdom

*Corresponding author: mnnx@leeds.ac.uk (Nan Xu) and A.Morina@leeds.ac.uk (Ardian Morina)

S1. Results and discussion

S1.1. Raman-based coating wear measurement

A schematic of Raman-based coating thickness quantification method under dry friction condition was shown in Figure S4. Here, silicon underlayer served as Raman signal provider due to its high intensity at 520 cm $^{-1}$ and the top a-C:H coatings were considered as light attenuating layer. Since light intensity will be attenuated in the a-C:H due to absorption (A) and reflection (R), Raman intensity of silicon signal (I_s) of silicon substrate depends on the transmittance values of both incident light (I_o) and scattered light, and is given based on Beer's law by

$$I_s = I_o \beta T_o T_1 \quad (1)$$

where β is light scattering rate, $I_o\beta$ is Raman intensity of silicon 1st band of silicon substrate, and T_o and T_1 are transmittance values of incident light and scattered light respectively. Additionally, it should be pointed that there exists shift of light wavelength on the sites of Raman scattering. When employing silicon as Raman signal provider, and the wavelength (λ_o, 488 nm) of incident light will shift to 500 nm (λ_1, scattered light), according to the equation:

$$\lambda_1 = \frac{1}{\frac{1}{\lambda_o} - \nu} \quad (2)$$

where ν is Raman shift. (520 cm $^{-1}$ for silicon 1st band).

By substituting the transmittance (T) in the equation (1) with the following expression:

$$T = (1 - R)^2 exp(-A) = (1 - R)^2 exp(-\alpha t) \quad (3)$$

where α is the absorption coefficient and t is the thickness of a-C:H coating (unit: μm), the relationship between I_s and t can be constructed by:

$$I_s = I_o \beta (1 - R_o)^2 (1 - R_1)^2 exp(-\alpha_o - \alpha_1) t \quad (4)$$

where R_o and α_o are the reflectivity and absorption coefficient of a-C:H for incident light (488 nm), and R_1 and α_1 are that for scattered light (500 nm). The thickness of a-C:H can be obtained through rearranging the equation (4) as the expression:

$$t = -\frac{1}{\alpha_o+\alpha_1} ln \frac{I_s}{I_o\beta(1-R_o)^2(1-R_1)^2} = \frac{-1}{\alpha_o+\alpha_1}[lnI_s - lnI_o\beta - ln(1-R_o)^2(1-R_1)^2] \quad (5)$$

With independently measurements of R_o, R_1, and $I_o\beta$, and obtaining the absorption coefficients, the thickness of a-C:H coatings can be calculated based on I_s. Here, the absorption coefficient (α) of a-C:H can be obtained by

$$\alpha = \frac{1}{-t} ln \frac{T}{(1-R)^2} \quad (6)$$

which derives from equation (3) and t is measured by optical profilometer.

To verify the accuracy of this Raman-based approach, a tribo-tested sample (90 mins) was investigated by comparing the results of Raman and optical profilometer. Figure S5 provides detailed information about the wear quantification process. For transmittance and reflectivity acquisitions, UV-vis-NIR spectroscopy was employed to characterize the samples with a-C:H deposited on glass plates, and the spectra in the wavelength region 400 to 600 nm were displayed in Figure S5a. Table S1 summarizes the optical parameters at wavelength of 488 and 500 nm. Then, a line-scanning Raman spectroscopy was conducted across the wear track as shown in Figure S6. The corresponding spectra of silicon are displayed in Figure S5b. The corresponding Raman intensity values of silicon bands were listed in Figure S5c (blue line). With obtaining all the required parameters in the equation (1), the coating thickness values across the wear track were obtained. After subtracting the thickness value of as-grown a-C:H, the wear profile curve was given in Figure S5c (green line) and compared with the result obtained by optical profilometer as shown in Figure S5d. It could be observed that the wear profile deriving from the Raman silicon signal compared well with that measured by optical profilometer (after depositing iridium layer). Therefore, this proposed approach could avoid measurement deviations caused by tribo-induced polishing effect and be directly used to provide accurate wear depth values under dry friction.

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

Thickness (nm)	T_o (%)	T_1 (%)	R_o (%)	R_1 (%)	α_o (cm^{-1})	α_1 (cm^{-1})
183.3±3.0	12.38	13.56	21.55	21.82	8.75×10^4	8.21×10^4
277.1±2.3	5.20	5.94	22.03	22.36	8.87×10^4	8.36×10^4

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

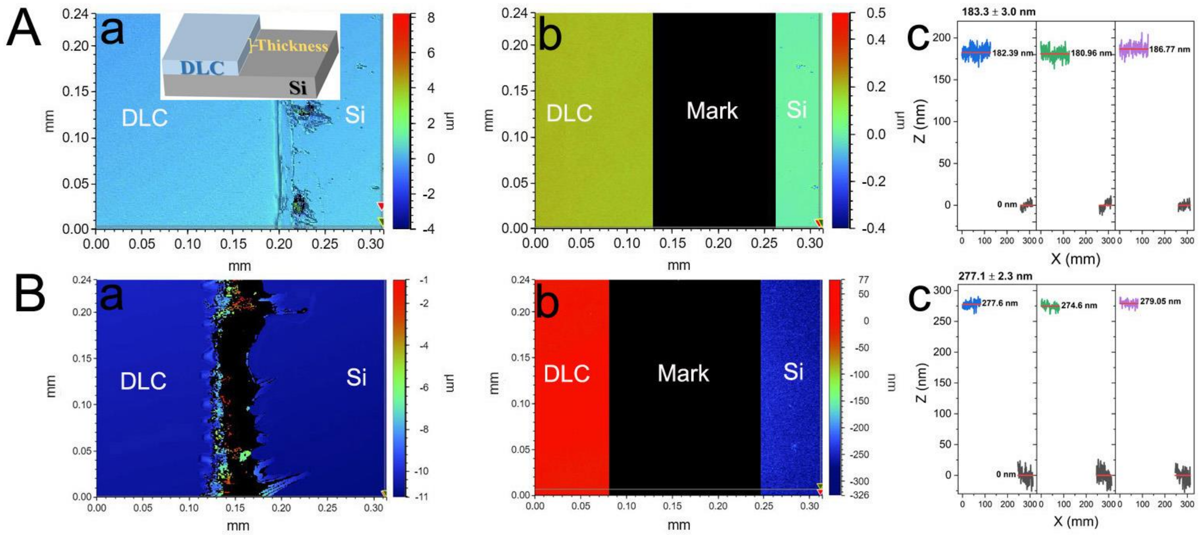

Figure S1. 3D optical microscopy images of samples with a-C:H coatings of different thickness deposited on Si wafers (A, 183.3 nm; B, 277.1 nm). (a) 3D optical microscopy images. (b) Images showing the marking areas. (c) Step height values showing the coating thickness.

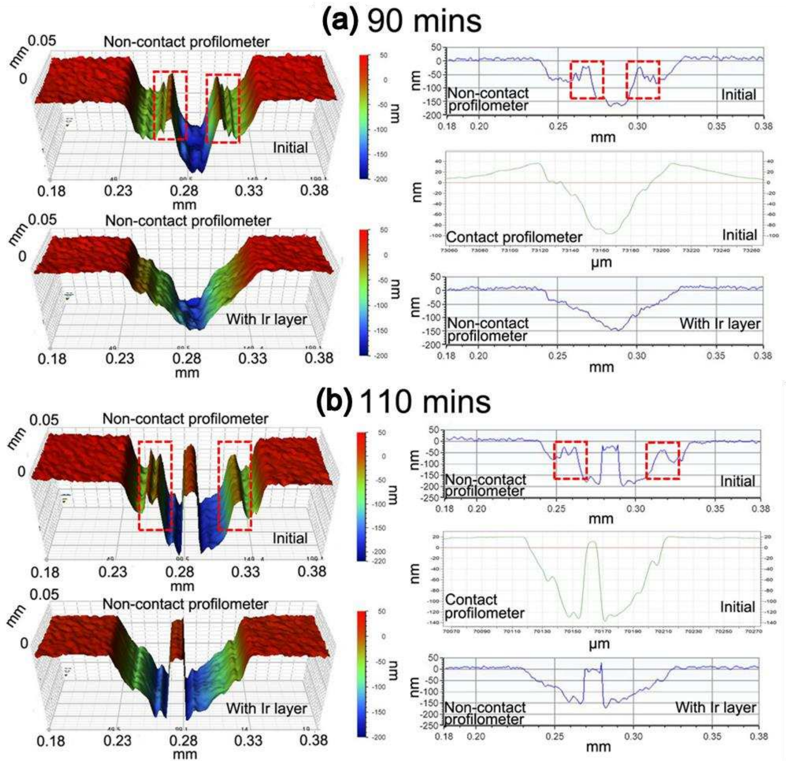

Figure S2. Comparison of wear profile curves obtained by non-contact optical profilometer (before and after depositing iridium layer on top of a-C:H) and contact profilometer for tribo-tested samples under dry friction (a, 1N, 90mins; b, 1N, 110mins). The marked areas indicated the measurement errors of optical profilometer (before depositing iridium layers).

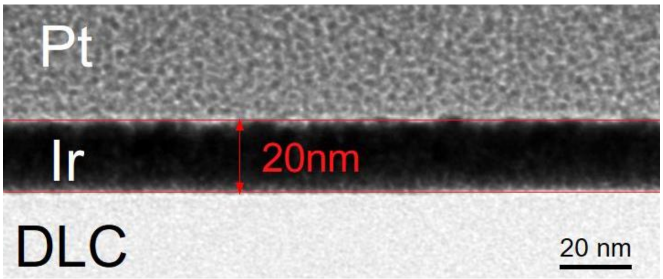

Figure S3. HRTEM image of cross-sectional morphology of the a-C:H surface with iridium and platinum layers. The thickness of iridium is ca. 20 nm which is employed to provide a top surface with consistent optical properties.

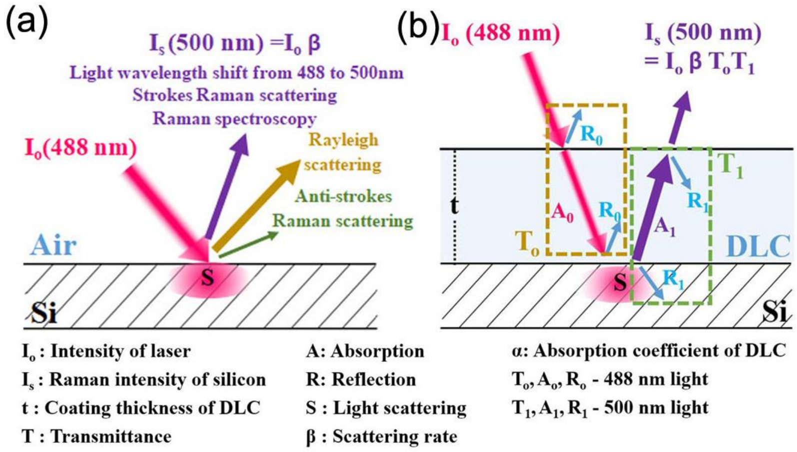

Figure S4. Schematic illustration of Raman-based coating thickness quantification method. (a) Light wavelength shift on the sites of Raman scattering. (b) Coating thickness quantification process under dry friction.

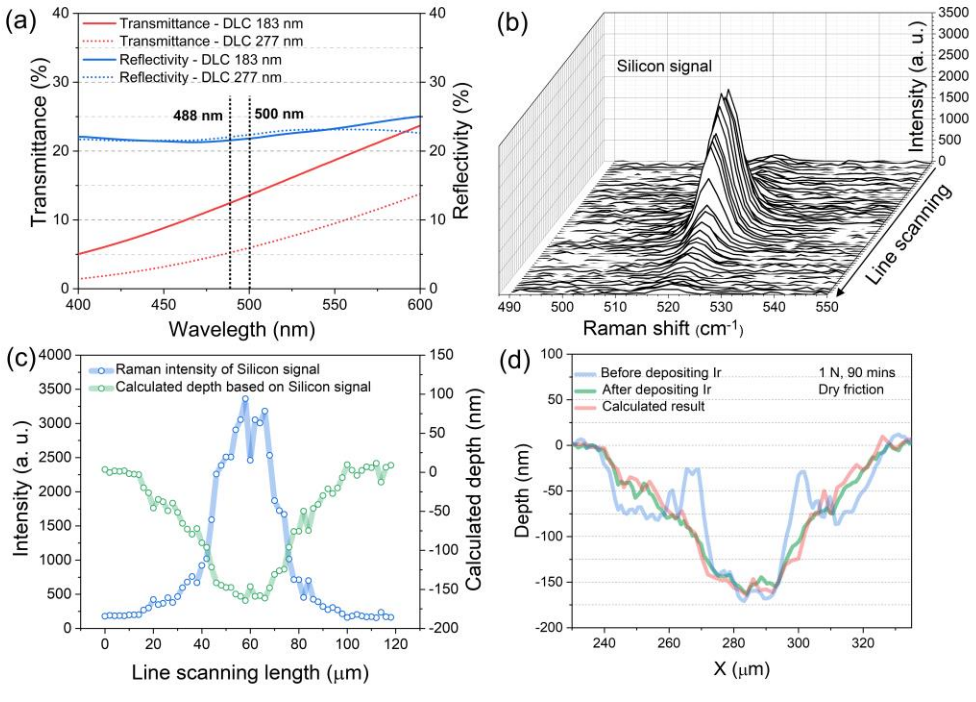

Figure S5. (a) Transmittance and reflectivity spectra of as-grown a-C:H films of different thickness deposited on glass substrate. (b) Raman spectra of a series of silicon bands obtained from line-scanning. (tribo-tested sample: 1N, 90 mins) (c) Intensity of silicon bands and calculated wear profile curve based on the Raman intensity of silicon signal. (d) Comparison between calculated wear profile derived from Raman intensity of silicon bands and measured wear profile characterized by non-contact optical profilometer (before and after depositing iridium layer on top of a-C:H).

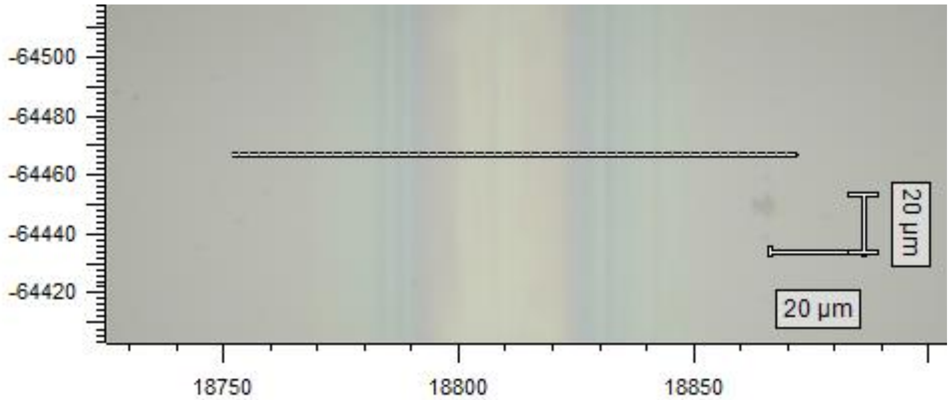

Figure S6. Optical image of line-scanning trace of Raman spectroscopy across the wear track (tribo-test time: 90 mins).

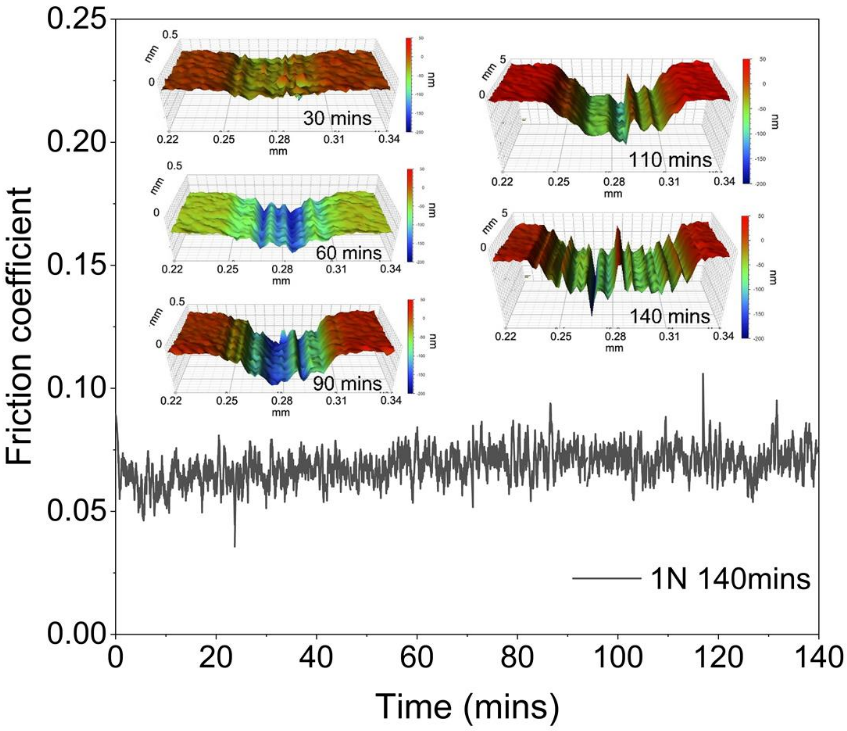

Figure S7. Friction behavior of a-C:H film under oil lubrication (PAO + 0.8 wt.% MoDTC) and 3D images of wear scars obtained by optical profilometer after depositing iridium layers.

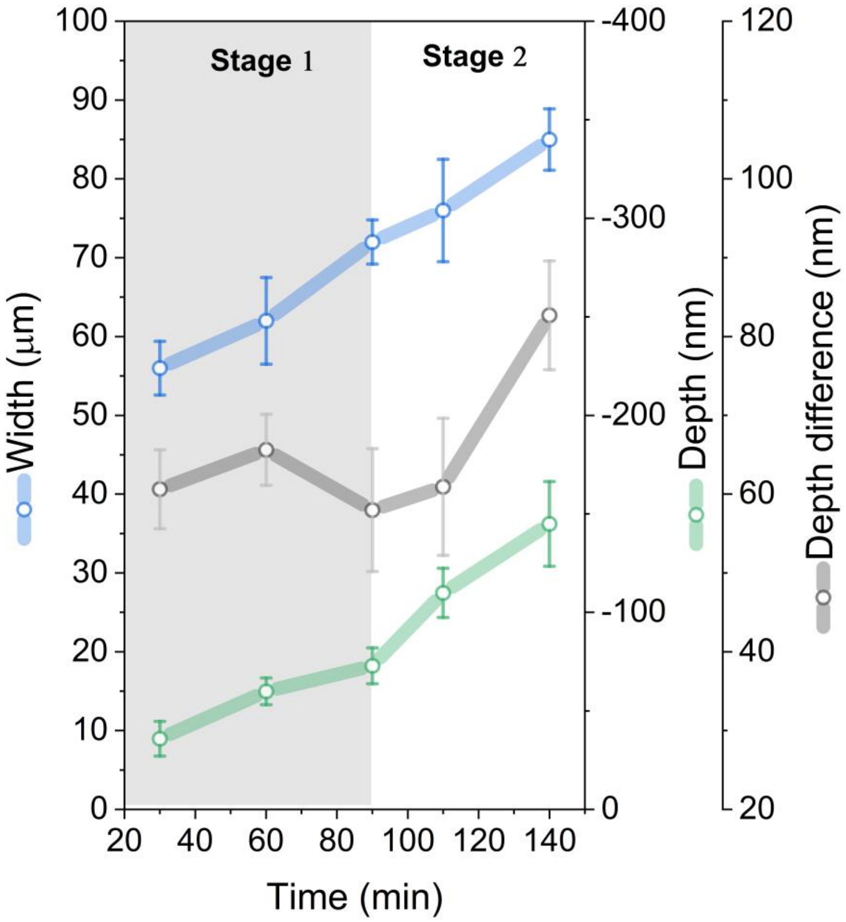

Figure S8. Evolution of width and depth of wear scars with test time under oil lubrication (PAO with 0.8 wt.% MoDTC, 1 N).