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Supplementary Information for

Towards superlubricity in nanostructured surface: the role of van der Waals forces

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Section A. Surface roughness and integrity of nanostructured carbon-based thin films

The surface roughness parameters were calculated by using the statistical tool in the Gwyddion software. The reported values are the root mean square (RMS) surface roughness measured by the AFM-topography images (scan area of 5 x 5 μm^2). This represents the standard deviation of the distribution of surface heights, so it is an important parameter to describe the surface roughness by statistical methods, as described in standard ASME B46.1. The mathematical definition and the digital implementation of this parameter are as follows:

$$RMS = R_q = \sqrt{\frac{1}{L}\int_0^L Z^2 \partial x} \approx \sqrt{\frac{1}{n}\sum_i^n Z_i^2}$$

where RMS (also known as R_q) is the root mean square average deviation of the roughness effective profile ordinates measured from the mean line, L is the length of the profile, $Z(x)$ is the function of the profile heights. This parameter is more sensitive than the arithmetic average height (R_a) to large deviation from the mean line.

The fractal dimension is a sophisticated parameter used to define the morphology of a surface, considering also the roughness. The surfaces analysis of the fractal dimension was obtained from the Cube Counting method[1] by using the fractal analysis tool implemented within the statistical data process in the Gwyddion software. This method of fractal analysis is directly derived from a definition of box-counting fractal dimension. The algorithm is based on the following steps: a cubic lattice with lattice constant (l) is superimposed on the z-expanded surface. Initially l is set at $X/2$ (where X is length of edge of the surface), resulting in a lattice of 2×2×2 = 8 cubes. Then $N(l)$ is the number of all cubes that contain at least one pixel of the image. The lattice constant is then reduced stepwise by factor of 2 and the process repeated until (l) equals to the

distance between two adjacent pixels. The slope of a plot of log($N(l)$) versus log($1/l$) gives the fractal dimension (D_f) directly.[2-5] From the definition of fractal dimension we have:[3]

$$D_f = \lim_{l \to 0} \left(\frac{\log N(}{\log (1/} \right.$$

Self-affinity (when parts of the fractal is statistically similar to the original) for different variations in scale is a generalization of self-similarity which is the basic property of most of the deterministic fractals. Many randomly rough surfaces are assumed to belong to the random objects that exhibit the self-affine properties and they are treated self-affine statistical fractals.

Section B. Chemical analysis

The in-depth chemical profiles of a-C:H thin films were obtained by glow discharge optical emission spectroscopy (GD-OES, Horiba GD-Profiler 2, pressure = 650 Pa and RF-power source = 15W). Figure S1 shows the in-depth chemical profile obtained by GDOES of the sample obtained with a gaseous mixture of 50% C_2H_2 and 50% H_2. It is clearly seen that there are three different chemical regions. The outermost region is the a-C:H film, where there is a high relative intensity of carbon and hydrogen, and a lower oxygen signal as contaminant. The junction or bonding region is the a-SiC_x:H:O buffer layer (the delimited region between dashed lines in Figure S1).Finally, the innermost region is the ferrous alloy. As expected from the used precursor, the interlayer is mainly constituted by carbon, silicon, hydrogen, and oxygen (also see the previous work by our group elsewhere).[6] At the top, a schematic helps to see the bi-layer system on carbon steel.

Section C. Mechanical properties

The hardness (H) and elastic modulus (E) were measured for the a-C:H thin films by using a nanoindentation system (MicroMaterials NanoTest-600), equipped with a three-sided pyramidal diamond tip (Berkovich indenter). Oliver and Pharr method[7] was used to analyze the indentation load-displacement data. The indentations were carried out at a depth of 100 nm in order to avoid the influence of the substrate on the measurements. A typical a-C:H thin film thickness is ~ 2 μm.

In our a-C:H thin films, the hardness is typically varies from 10 to 20 GPa[8] and the elastic modulus varies from 60 to 210 GPa.[9] As presented in Table S1, both the hardness (H) and elastic modulus (E) monotonically decrease with the increasing of the H/C ratio. However, neither hardness nor elastic modulus may be separately used as suitable parameters for predicting analysis of elastic and plastic deformation mechanisms. In particular, the elastic strain to failure is related to the H/E ratio to analyze the resistance to elastic deformation and the H^3/E^2 ratio to analyze the resistance to plastic deformation in determining coating performance.[10] Whereas, the higher the H/E ratio (higher elastic strain), the higher the energy dissipation, and the higher the H^3/E^2 ratio (higher fracture toughness) the lower the energy dissipation. Thus, it is mandatory a detailed analysis of both ratios in order to determine the real contribution of mechanical properties on the friction coefficient.

As shown in Figure S2, the H/E ratio decreases as a function of the H-content. Considering the slope, the H/E ratio diminishes up to 2%, representing a lower value than the experimental error (lower than 10%). This experimental fact indicates that the lower dissipation energy through an elastic deformation mechanism (less wear resistance) must be expected for the a-C:H thin films with the highest H-content (S90, 10% C_2H_2: 90% H_2). This effect is also observed for the plastic regime, as shown in Figure S3, the H^3/E^2

ratio slightly decreases as a function of the H-content in these types of loaded contact. Considering the slope, the H^3/E^2 ratio diminishes up to 10%, representing a value similar than the experimental error (lower than 10%). Thus, the lower H^3/E^2 ratio prompts more energy dissipation that should induce a higher coefficient of friction. Such an interpretation is not corroborated because we observed that the coefficient of friction decreases with the increasing of the H-content.

Finally, Figure S4 shows a sequence of FEG-SEM images (Tescan, MIRA3 model) of two different unidirectional sliding measurements. At the top, one sliding trail was performed by using a normal applied force of 500 mN (high value). One can see that a plastic deformation mechanism (sink-in effect) of the a-C:H thin film took place. At the bottom, five sliding trails were performed by using a normal applied force of 10 mN (the same value used in our friction experiments). One can see that no plastic deformation mechanisms are apparent. Thus, the friction forces measured by nanoindentaion followed by unidirectional sliding do not contain effects of energy dissipation through plastic deformation mechanisms.

Section D. Topography and surface parameters

Figures S5 a/b and c/d show the 2D-top view/3D-topography AFM images (scan area of 2 x 2 μm^2) for the untreated substrate (as polished) and the sample deposited with C_2H_2 only (H/C = 1), respectively, obtained in non-contact mode. One can see that the topography of both samples (as polished and after a-C:H thin film deposition) is rather different. Thus, the nanostructured surface of valleys and hills is characteristic for the a-C:H thin films.

Surface roughness is very important for many fundamental problems such as friction, contact deformation, heat and electric current conduction, tightness of contact

joints and positional accuracy.[11] The surface profile is characterized by slowly varying components (texture and waviness) with the short-scale roughness on top of it. For this surface profile, the RMS roughness of the a-C:H thin films, obtained by subtracting the waviness form the original profile (texture), is characterized by RMS roughness amplitude values from 1.6 to 2.0 nm, as demonstrated in Figure S6. The roughness mean line is the line that divides the profile so that the sum of the squares of the deviation of the profile height from it is equal to zero. Therefore, a hydrogen addition to acetylene discharges can influence the electrical properties of intercalation materials modifying to height and spacing parameters related to surface roughness due to an increased bond saturation of gas phase radicals and ions by atomic hydrogen.[12] Being an interpretation that was not corroborated, the RMS roughness profiles are similar for the all a-C:H thin films, without significant variation in the hydrogen addition.

The surface morphology of nanostructured carbon films is characterized qualitatively by its roughness and its fractal dimension.[2, 4] Figure S7 shows the fractal dimension line profile of the self-affine random surfaces via AFM images. The fractal dimension corresponds to the slope of adjustment line of the log(N(l))/log(1/l) graph (box count/box size). For self-affine surfaces is usually established that the statistical properties of their morphology are invariant under the scaling modification.[13, 14] The fractal nature in patterns of electrostatic potentials and topography maps of the scan area (5 x 5 μm^2) as function of the hydrogen-to-carbon (H/C) ratio at different H_2/C_2H_2 mixture can show the correlation the electrostatic contribution and friction behaviour on the surface morphology of a dielectric thin film. Fractal dimension line profiles in topography and electrostatic potentials maps for the a-C:H thin films are independent of the hydrogen addition, consequently the nanophysical contacts depend on the electrical field of induced dipoles established by the fractal nature of the load distribution patterns.

Section E. Lateral force microscopy: calibration and measurements

Lateral or friction force microscopy (LFM/FFM) is typically used in nanoscratch and surface friction measurement based on atomic force microscopy (AFM).[15, 16] It instead of measuring the horizontal deflection of the photodetector signal, it measures its lateral deflection. When measuring torsional deformation of the AFM cantilever that results from the lateral forces acting between tip and sample surface,[17] the photodetector signal can be calibrated/converted into units of force. An impediment for the quantification of lateral forces in AFM, however, is the lack of reliable and established calibration methods.[18] A widespread acceptance of LFM requires quantification coupled with a solid understanding of error significance in the calibration factors. In this paper we consider the wedge calibration method for quantitative lateral force measurement in AFM, been first proposed by Ogletree et al.[19] developed to experimentally determine the lateral force response of a cantilever as a function of applied load (error in the calibration factors obtained was found to be ca. 5%), and revised by Varenberg et al.[20] and later by Asay and Kim[21, 22]. The wedge method it is based on comparing the lateral and normal force signals on surfaces with well-defined slopes, and differs from the others calibration methods in several aspects (e.g., this method assumes that the width of the wedge is significantly larger than the tip radius, so that does not require knowledge of the shape of the tip). The wedge calibration method is probably the most commonly accepted one, fits for integrated probes with sharp tips only and was performed on a complex specially prepared calibration grating.[23]

For the calibration, a standard sample grating with sloped and flat facets (211-37643-01 supplied with Shimadzu SPM-9700) was swept in contact mode at angle 90° on different loads (normal forces). The standard sample (soda glass, gold coating) consists

of a two-dimensional network with grooves number of 1000 ±5 grooves/mm, depth of groove of 100 ±20 nm and side wall angle θ = 26.25°.

The initial step for LFM calibration by the wedge method is the determination of the force-distance curves (*f-d curve*). This allows converting the horizontal deflection signal into a normal force F_N by the normal deflection sensitivity S (V/m) that is then defined as the slope of the *f-d curve* between the tip and incompressible sample surface as show Table S2. In this way, the normal force acting between the tip and the sample can be calculated as:

$$F_N = \frac{k.(V_N)}{S}$$

where k (N/m) is the spring constant of the cantilever (~ 0.36 N/m) and V_N (Volts) is the photodiode output signal.

For the calculations, two parameters are extracted from each scan line, the half-width friction loop $W(L)$ and the offset friction loop $\Delta(L)$. Both parameters are linear functions of the normal force F_N and experimentally, the slopes $W' = \partial W/\partial L$ and $\Delta' = \partial\Delta/\partial L$ extracted from the friction loops under different normal forces are used in the calculation of the calibration factor α as follows:[19, 20]

$$\alpha\Delta_0^{'} = \Delta' = \frac{(1+\mu^2).\sin\theta.\cos\theta}{\cos^2\theta - \mu^2.\sin^2\theta}$$

$$\alpha W_0^{'} = W' = \frac{\mu}{\cos^2\theta - \mu^2.\sin^2\theta}$$

$$\mu + \frac{1}{\mu} = \frac{2\Delta_0^{'}}{W_0^{'}.\sin 2\theta}$$

where bi-directional lateral force loops are drawn for flat, positively tilted W_0 and negatively tilted Δ_0 surfaces (more details on the schematic friction loops are displayed

in Fig. 6 of this supplementary reference[19]). To overcome the problem of the uncertainty of the torsion signal is zero point, we used a simpler procedure than that used in the original method as proposed by Varenberg et al.[20]

Figure S8 a to d show a summary of the calculations and procedures for the wedge method by sweeping the standard sample with the same V-shaped cantilever model and the silicon nitride tip with gold coated used in LFM measurements (OMCL-TR800PSA-1, Olympus). The calibration factor required to convert the lateral deflection signal (Volts) into force units (Newtons) is 1800 nN/V.

All LFM measurements were performed on scanning probe microscope (Shimadzu SPM-9700). Figure S9 a to e show the 2D-topography AFM images (on the left) and friction force images (on the right) obtained by LFM contact mode for samples a-C:H thin film containing different H/C ratio at the outermost layer. The frictional forces were obtained from the LFM images with a resolution of 512 x 512 pixels taken at 0.25 Hz scan rate, 2 μm x 2 μm scan size and 2V operating point. The average friction force of each sample was calculated from the obtained calibration factor.

Supplementary Figures

Figure S1 In-depth chemical profiles of the a-C:H thin film (S50, 50% C_2H_2: 50% H_2) by GD-OES. In addition, a schematic describes the a-C:H/a-SiC_xH:O/ferrous alloy as a sandwich structure.

Figure S2 H/E index as a function of the hydrogen-to-carbon ratio in a-C:H thin films.

Figure S3 H^3/E^2index as a function of the hydrogen-to-carbon ratio in a-C:H thin films.

Figure S4 Sequence of FEG-SEM images of two different unidirectional sliding measurements. At the top, one sliding trail was performed by using a normal applied force of 500 mN (high value) where plastic deformation as sink-in took place. At the bottom, five sliding trails were performed by using a normal applied force of 10 mN (the same for friction measurements) where no plastic deformation mechanisms are apparent.

Figure S5 Comparison of 2D-top view/3D-topography from untreated substrate (a + b) and substrate deposited (c + d) at H/C ratio = 10 (10% C_2H_2:90% H_2).

Figure S6 Comparison of RMS surface roughness of the a-C:H thin films obtained at different H_2/C_2H_2 mixtures.

Figure S7 Comparison of area-scale profiles of fractal dimension (D_f) between the topography and electrostatic potentials maps.

Figure S8 (a-d) Some steps of lateral force wedge calibration procedure. (a) 3D-Topography of standard sample - precision grid plate and (b-c) lateral signal loop (and topography) as function of distance from a scan line under normal deflection signal of 2V (i.e., normal force of 43.2 nN); (d) Normal force estimative by *f-d curve* of standard sample. The calibration factor of 1800 nN/V is determined through the half-width friction loop W(L) and the offset friction loop Δ(L) as function of normal force used.

Figure S9 (a-e) 2D-topography AFM images (on the left) and LFM images (on the right) of the a-C:H thin films deposited at various H/C ratios = 1 (a); 1.33 (b); 2 (c); 4 (d); and 10 (e) (scan area of 2 x 2 μm^2).

Supplementary Tables

Table S1 Hydrogen effect on mechanical properties measured in the nanostructured surface of a-C:H thin films.

Samples(Surface hydrogen-rich a-C:H films grown in)	H (GPa)	E (GPa)	H/E (elastic deformation index)	H^3/E^2 (plastic deformation index)
S0 (100% C_2H_2)	14.4 ± 0.5	122 ± 8	0.12 ± 0.01	0.20 ± 0.05
S25 (75% C_2H_2: 25% H_2)	13.5 ± 0.5	120 ± 7	0.11 ± 0.01	0.17 ± 0.04
S50 (50% C_2H_2: 50% H_2)	12.6 ± 0.5	114 ± 5	0.11 ± 0.01	0.15 ± 0.04
S75 (25% C_2H_2: 75% H_2)	11.5 ± 0.5	110 ± 5	0.10 ± 0.01	0.13 ± 0.03
S90 (10% C_2H_2: 90% H_2)	10.9 ± 0.5	109 ± 6	0.10 ± 0.01	0.11 ± 0.03

Table S2 Normal force estimative by *f-d curve* of standard sample through normal deflection sensitivity S = 0.01675 V/nm.

Normal deflection signal (V)	Normal force (nN)
0.25	5.4
0.5	10.8
1	21.6
2	43.1
3	64.7
4	86.3
5	107.8

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