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## Self-adaptive and self-healing nanocomposite tribocoatings

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# CHAPTER 4

## On the S/W stoichiometry and triboperformance of $WS_xC(H)$ coatings deposited by magnetron sputtering\*

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In this chapter,  $WS_xC(H)$  coatings were deposited on single crystal silicon(100) wafers by magnetron co-sputtering and reactive sputtering at various target-substrate distances. Upon increasing the distance, the stoichiometric S/W ratio increases from 0.51 to 1.89. Also, the porosity of coatings gradually augments and a columnar microstructure tends to form. Preferential sulfur resputtering rather than contaminations primarily accounts for the low S/W ratio. TEM reveals randomly oriented  $WS_2(002)$  platelets in the  $WS_xC$  coatings when deposited at a large distance, which is supported by XRD. The composite coatings exhibit a decreasing hardness and elastic modulus with increasing target-substrate distance. The triboperformance is strongly affected by the coating composition, the target-substrate distance and the testing environment.

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## 4.1 INTRODUCTION

WS<sub>2</sub> belongs to the class of layered transition metal dichalcogenides (TMD) and has drawn considerable attention owing to its excellent solid lubrication properties. WS<sub>2</sub> crystallizes in the hexagonal structure where a layer of tungsten atoms is sandwiched between two hexagonally packed sulphur layers. While the bonding within the layer is covalent, the bonding between the adjacent layer consists of weak Van der Waals interactions [1]. The electronic structure of this TMD results in a small positive net charge outside of the lamellae, leading to an electrostatic repulsion between the (002) hexagonal basal planes and thus offering an easy planar glide [2]. In fact, sliding can readily shear TMD crystals to generate clean and atomically smooth surfaces [3]. Even amorphous WS<sub>2</sub> can be crystallized and basal planes are realigned along the sliding direction, offering an ultralow coefficient of friction (CoF) [4,5]. Therefore, sputtered TMD coatings have been widely used in transport industry, particularly in high vacuum aerospace environment [6,7]. However, TMDs' lubricating properties usually degrade through oxidizing in moisture and are also limited by their low bearing capacity. Various third elements (e.g. Ti [8], Cr [9], Al [10], Pb [11], Ni [12], C [13]) were incorporated to reduce oxidation and improve the triboperformance. Among them, the nanocomposite MeY<sub>2</sub>/a-C coatings (where Me is Mo or W, and Y is S or Se), namely MeY<sub>2</sub> lamellae embedded in an amorphous diamond-like carbon (DLC) matrix, have demonstrated excellent tribological characteristics, with both a low CoF and a high wear resistance over a wide range of humidities [14,15]. Voevodin et al. [15,16] even pioneered a "chameleon" WC/WS<sub>2</sub>/DLC coating, where WS<sub>2</sub> aims at providing low friction in dry atmospheres, while the carbon matrix provides low friction in humid environments.

One negative aspect of magnetron sputtering high-quality MeY<sub>2</sub>/a-C coating is that the MeY<sub>x</sub>/a-C is usually sub-stoichiometric, with  $x < 2$  [6,17] and this potentially impairs the tribological behaviors, for instance created by the sulfur deficiency in a MeS<sub>2</sub>/a-C coating. Voevodin *et al.* [6] indicated that the WS<sub>2</sub>/a-C composite with sulfur content < 15 at.% had a surprisingly high CoF of 0.5-0.7 in vacuum and 0.2-0.3 in dry nitrogen, consistent with the tribological behavior of single-phase unhydrogenated DLC in vacuum. A low Y/Me ratio is generally attributed to the preferential resputtering of Y due to the bombardment of energetic particles reflected on the coatings [18-21] and the reactions between MeY<sub>2</sub> and the residual atmosphere (e.g. H<sub>2</sub>, O<sub>2</sub>) [17,20,22]. For instance, several studies [17,20] showed that sputtering with a H-containing gas is detrimental for the S/W ratio due to H contamination through the H+S→H<sub>2</sub>S reaction. In comparison, it was also reported that a sulfur deficit can be compensated by using an Ar-H<sub>2</sub>S sputtering atmosphere. For instance, stoichiometric TMD layers or layers with excess sulfur can be achieved by reactive sputtering a MeY<sub>2</sub> or Me target with a fairly low H<sub>2</sub>S pressure [23,24] or sulfurization of MO<sub>3</sub> films in an H<sub>2</sub>S atmosphere [25].

It has been well established [26–28] that the sputter-deposition parameters influence the stoichiometry, microstructure and mechanical properties of TMD tribocoatings. However, previous studies have not examined the influence of target-substrate distance in much details. The present study concentrates on the influence of the target-substrate distance on the microstructure, composition, stoichiometry, mechanical and tribological performance of  $WS_xC(H)$  coatings deposited by either a reactive or a co-sputtering process.

## 4.2 EXPERIMENTAL PROCEDURES

### 4.2.1 Preparation of the $WS_xC(H)$ coatings

All  $WS_xC(H)$  coatings were deposited on single crystal silicon(100) wafers. The substrates were first ultrasonically cleaned in acetone followed by Ar plasma etching for 20 min at pulsed direct current (p-DC) with -400 V bias voltage at 250 kHz and 87.5% duty cycle. The PVD power units for sputtering were operated in a current-control mode. A current of 0.5A was applied to two  $WS_2$  targets (p-DC) at 150 kHz pulse frequency (70 % duty cycle). For reactive sputtering of  $WS_xCH$  coatings, different gas flow ratios, namely  $Ar:C_2H_2 = 15:10$  sccm (referred to group S1 hereafter) and  $Ar:C_2H_2 = 20:5$  sccm (referred to group S2 hereafter) were used to alter the carbon content. The unhydrogenated  $WS_xC$  coatings were deposited by co-sputtering two  $WS_2$  targets and one graphite target (DC) in pure Ar atmosphere (25 sccm, referred to group S3 hereafter). To study the effect of the target-substrate distance on the S/W stoichiometry, microstructure and triboperformance, each group of coatings was deposited at 70, 145, 220 and 290 mm distance away from the targets. This combination leads to a total of 12 coatings with different compositions. The coatings are hereafter referred to as  $S_x-D_y$ , with  $S_x$  ( $x = 1, 2, 3$ ) indicating the flow rate of  $C_2H_2$  gas (10, 5, 0 sccm) and  $D_y$  ( $y = 70, 145, 220, 290$  mm) indicating the target-substrate distance in the deposition. As an example, S1-D70 refers to the coating deposited at a target-substrate distance of 70 mm by reactive sputtering with  $Ar:C_2H_2 = 15:10$  sccm. A 25 sccm gas flow rate corresponds to a total pressure of around 0.6 Pa. A pure Cr (99.9%) target was powered by a Pinnacle 6/6 kW DC power to produce a Cr interlayer for enhancing coating interfacial adhesion. The coating deposition time was kept at 2h for all samples. The substrates were self-biased using a floating potential. The base pressure of the chamber before deposition was  $3-5 \cdot 10^{-4}$  Pa. The substrates were mounted vertically on a carousel that was rotated at 3 rpm in front of the targets. No additional substrate heating was applied during deposition.

### 4.2.2 Characterization of the $WS_xC(H)$ coatings

The microstructure was investigated using an environmental scanning electron microscope (ESEM, FEI FEG-XL30) and a high resolution transmission electron

microscope (HR-TEM, 2010F-JEOL). Energy dispersive X-ray spectroscopy (EDS, EDAX Octane Silicon Drift Detector) with an accelerating voltage of 20 kV in FEI XL30 ESEM was employed to determine the chemical composition of the coatings. Note that EDS results are averaged by accumulating the signal from the same size spot for 100s on three random areas of each sample, with an error of 1 at.%. The grazing incidence X-ray diffraction (GI-XRD) spectra were collected with a PANalytical-X'Pert MRD to determine the crystalline phases of the coatings using a 2° incident angle in parallel beam geometry. X-ray photoelectron spectroscopy (XPS) was performed to investigate the elemental composition and possible chemical bonding of the fresh coatings, using a Surface Science SSX-100 ESCA instrument with a monochromatic Al K $\alpha$  X-ray source ( $h\nu = 1486.6$  eV). During data acquisition, the pressure in the measurement chamber was kept below  $2 \times 10^{-7}$  Pa. The electron takeoff angle with respect to the surface normal was 37° and the diameter of the analyzed area was 1000  $\mu\text{m}$  and the total experimental energy resolution was set to 1.16 eV. The XPS spectra were analyzed using the least-squares curve fitting program (Winspec, developed at the LISE laboratory of the Faculté's Universitaires Notre-Dame de la Paix, Namur, Belgium). Binding energy was reported to  $\pm 0.1$  eV [29]. The hardness and elastic modulus of the composite coatings were measured by a MTS Nano indenter XP® equipped with a diamond Berkovich tip. The indentation depth was fixed at 150 nm, i.e., about 10% of the coating thickness, to avoid the influence of the substrate. Raman spectra on the wear tracks were acquired by Thorlabs HNL equipped with a HeNe laser (632.8 nm), at approximately 1-2 mW in the range 200 - 2000  $\text{cm}^{-1}$ .

The tribological properties of the coatings were investigated at room temperature using a ball-on-disk CSM tribometer, with a 100Cr6 steel ball (6 mm in diameter) at a sliding speed of 10 cm/s. The ball slides against the coating under a normal load of 5N, resulting in a Hertz contact pressure of about 0.75 GPa. All samples were tribotested in both dry air (relative humidity of 5%,  $R_H$ ) and in humid air (55%  $R_H$ ) respectively, modulated by a home-made humidity adjustor. All wear tests were repeated twice for 10000 laps unless catastrophic failure occurred. After the wear tests, the wear tracks of the coatings and the wear scars of the ball counterparts were characterized by optical microscope. 3D confocal micrographs of the wear tracks were captured to measure the wear volume in order to evaluate the wear rates ( $W_R$ ). Normalized wear rates ( $\text{mm}^3 \text{N}^{-1} \text{m}^{-1}$ ) were then calculated through a Matlab code according to the following equation:  $K = V/(L \times s)$ , where  $V$  is the wear volume,  $s$  the total running distance of the ball over the disk, and  $L$  the normal load. To unveil the self-lubrication mechanism, a focused ion beam (FIB, Lyra Tescan, Czech) was applied to prepare lamellae in-situ on the wear tracks for cross-sectional TEM analysis.

### 4.3 RESULTS AND DISCUSSIONS

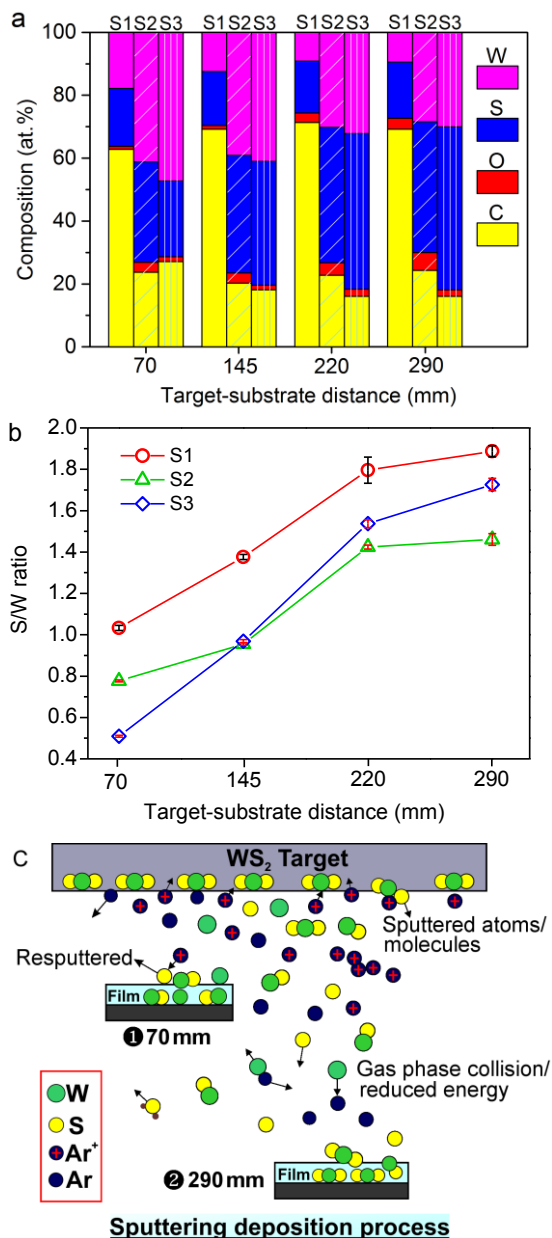
### 4.3.1 Chemical composition and structural characterization

**Figure 4.1a** shows that the chemical composition of sputtered WS<sub>x</sub>C(H) coatings changes upon target-substrate distance from 70 mm to 290 mm. EDS results inform on the atomic percentage of W, S, O and C excluding H, and EDS area mappings (not shown) indicated compositional homogeneity over the entire coating samples. As can be seen, the S1 group of coatings deposited with a high C<sub>2</sub>H<sub>2</sub> flow rate have a high carbon content up to 60 - 70 at.% C, while the S2 and S3 coatings have a rather low C content of 16 - 27 at.%. Due to residual oxygen in the PVD chamber, around 1-6 at.% oxygen is incorporated in the coatings and the higher oxygen content corresponds to the longer target-substrate distances. Increasing the target-substrate distance leads to a remarkable increase in S content and a decrease in W content for S2 and S3 coatings, while in the coating S1 the S content does not change much, but the W content decreases significantly.

**Figure 4.1b** shows the S/W ratio as a function of the target-substrate distance for the three types of coatings. S/W is seen to increase almost linearly with target-substrate distance, i.e., from 0.51 in S3-D70 to 1.89 in S1-D290. At the shortest target-substrate distance of 70 mm, the hydrogenated S1 and S2 coatings both show a higher S/W ratio than the unhydrogenated coating S3. Similar results have been reported for WSeC coatings [20], where WSe<sub>2</sub> deposited by reactive sputtering in CH<sub>4</sub> atmosphere showed a much higher Se/W ratio than that co-sputtered with a graphite target. Dimigen [26] and Goeke [30] pointed out that plasma decomposition of H<sub>2</sub>S even provides a controllable amount of sulfur to the growing film and allows to mitigate substoichiometry.

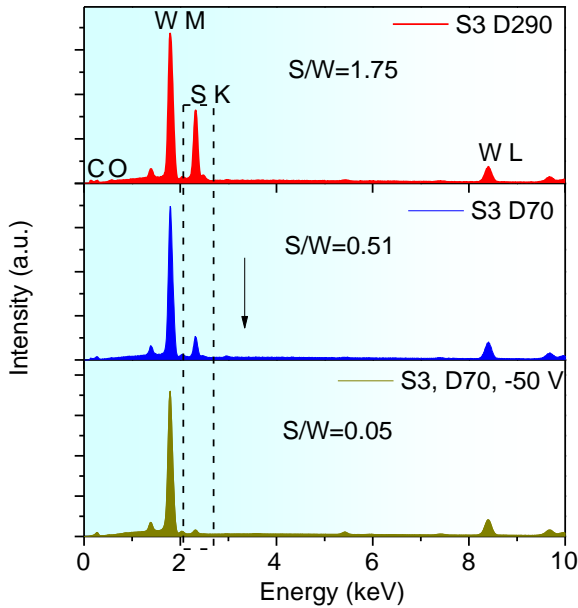
By combining Monte Carlo simulations and experiments to investigate the compositional variations of sputtered WS<sub>2</sub>, Sarhmmar *et al.* [21] proposed that the S/W ratio varies significantly with the processing pressure as well as with the position of substrates relative to the targets because of the different scattering behaviors of S and W in the gas phase. Indeed, the processing pressure determines the mean free path of the species and thus changes the frequency of scattering and collisions, thereby controlling the energy delivered to the growing coatings [21,26,31] by the impinging atoms/ions. A lower pressure yields substantial sulfur resputtering (low S/W ratio) due to enhanced energetic particle bombardment [32]. Since the total flow rate of gases in all the coatings investigated was kept at 25 sccm, the pressure can be estimated as being roughly the same. The deposition process is schematically depicted in **Figure 4.1c**. The higher S/W ratio at larger target-substrate distance stems from more frequent collisions which lead to more scattering of large atoms such as W and to a reduction of the energy of the particles on their way to the substrate. Consequently less S resputtering of the growing film occurs. Such preferential resputtering was further confirmed by applying a bias substrate voltage of -50 V for coating S3-D70, which significantly decreased the S/W ratio from 0.51 to almost zero (see **Figure 4.2**),

in agreement with Ref. [33]. Conversely, for a  $WS_x/a-C$  multilayer film a higher  $a-C/WS_x$  thickness ratio generates a higher  $S/W$  ratio because the  $a-C$  layer on top of the  $WS_x$  layer prevents the latter from being bombarded and hence from losing sulfur [34].



**Figure 4.1.** (a) Atomic composition of each coating indicated; (b) increasing  $S/W$  ratio with increasing target-substrate distance; (c) schematic of sputtering deposition process. Note that  $H$  is excluded for compositional analysis.

According to Ref. [35], momentum and energy are transferred in the collisions from the moving particles (Ar species) to the stationary target atoms (deposited W, S on the substrate). The reduction in energy relies on the masses of incident and target atoms. Assuming a scattering angle of  $\theta = 180^\circ$ , the energy transfer ratio  $K = \frac{4 M_1 M_2}{(M_1 + M_2)^2}$ , where  $M_1$  and  $M_2$  refer to the mass of energetic incident and rest target atom, respectively. When the masses are identical,  $K$  equals unity and the larger mass difference, the lower  $K$  will be. The atomic masses of Ar, S and W atom are 40, 32 and 184 respectively, so that the light S atoms (close to Ar) deposited on the substrate are more easily resputtered than W atoms. Also, S has a high vapor pressure (e.g.  $\sim 3 \times 10^{-4}$  Pa at room temperature) [30] and binds weakly to the substrate. On the other hand, the heavier W atoms cannot move far from the target after being sputtered, and this also accounts for the higher content of W in the coatings deposited at shorter target-substrate distances and the enrichment of S in the coatings deposited at longer target-substrate distances. It should be stressed out that the target-substrate distance, negative bias voltage (see **Figure 4.2**), deposition pressure (determining the mean free path of the species) and large S-W atomic mass difference all matter in determining S/W ratio of WS<sub>x</sub>C(H) coatings.

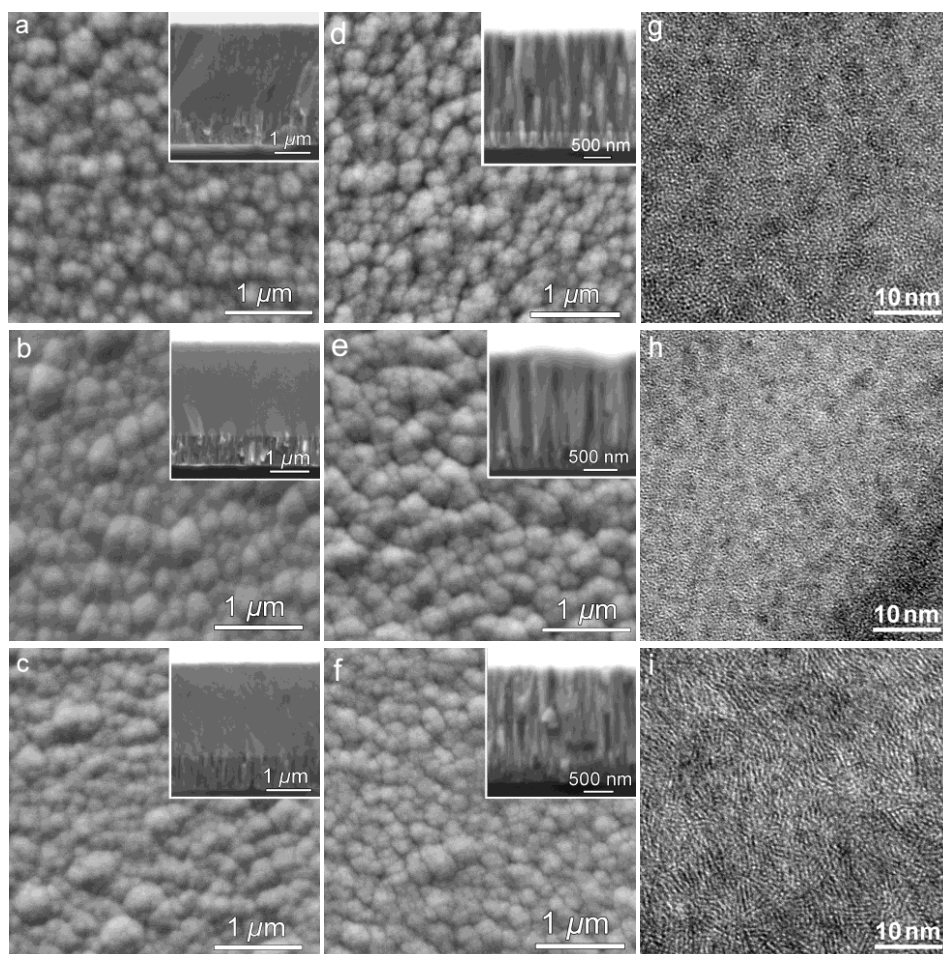


**Figure 4.2** Typical EDS spectra comparing S/W ratio as a function of target-substrate distance and negative bias voltage.

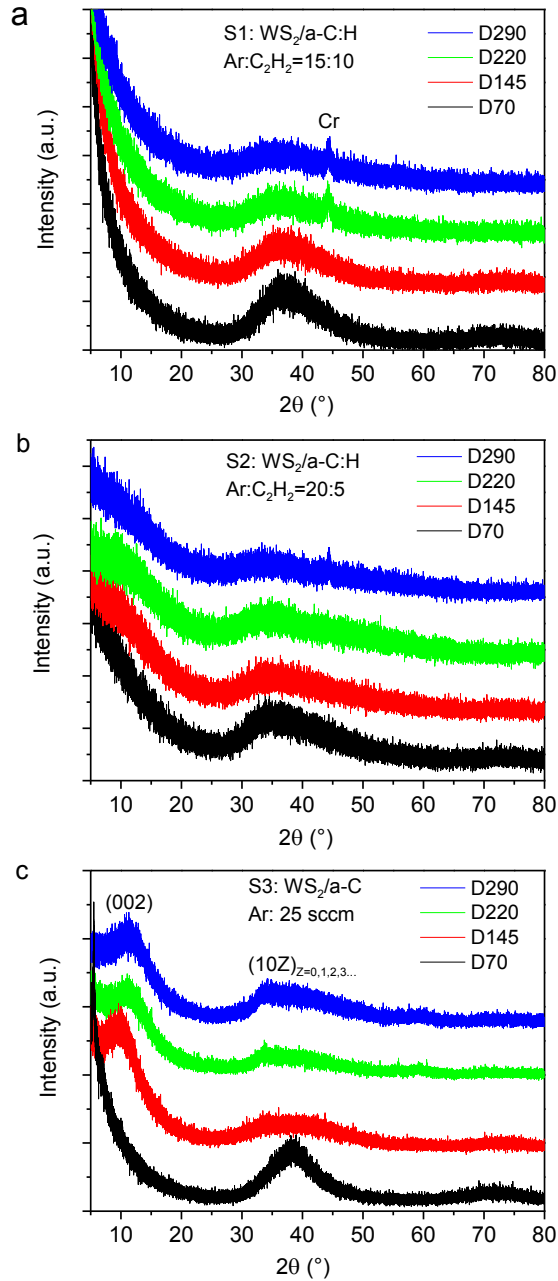
**Figure 4.3a-f** present the SEM images of S1-S3 WS<sub>x</sub>C(H) coatings deposited at the target-substrate distance of 70 and 290 mm, respectively. The WS<sub>x</sub>C(H) coatings were found to be structurally similar to typical cauliflower-like PVD sputtered DLC coatings.



The insets of **Figure 4.3a-c** present the corresponding fractured cross-section images, which clearly indicate that the coatings deposited at a target-substrate distance of 70 mm, whether by cosputtering or reactive sputtering, exhibit a dense and featureless microstructure. In contrast, the insets of **Figure 4.3d-f** show that WS<sub>x</sub>C(H) coatings deposited at a target-substrate distance of 290 mm become less compact and present columnar-like structures. HR-TEM images presented in **Figure 4.3g** and **h** show that the reactively sputtered coatings S1 and S2 both present a quasi-amorphous structure, although some short WS<sub>2</sub> platelets are apparent in the S-rich coating S2-D290. The HR-TEM image of the non-reactive sputtered coating S3-D290 presented in **Figure 4.3i** exhibits dense nanocrystalline WS<sub>2</sub> platelets of 10 nm length, randomly incorporated in an amorphous carbon matrix.



**Figure 4.3.** (a-c) S1-S3 coatings deposited at a target-substrate distance of  $D = 70$  mm; (d-f) S1-S3 coatings deposited at  $D = 290$  mm; (g-i) HR-TEM images of (d-f) respectively.



**Figure 4.4** GI-XRD spectra for coatings under different target-substrate distances: (a) S1; (b) S2; (c) S3.

**Figure 4.4** shows the GI-XRD patterns of the  $WS_xC(H)$  coatings. The patterns are similar; each coating is characterized by an asymmetrical (100) peak (edge plane)

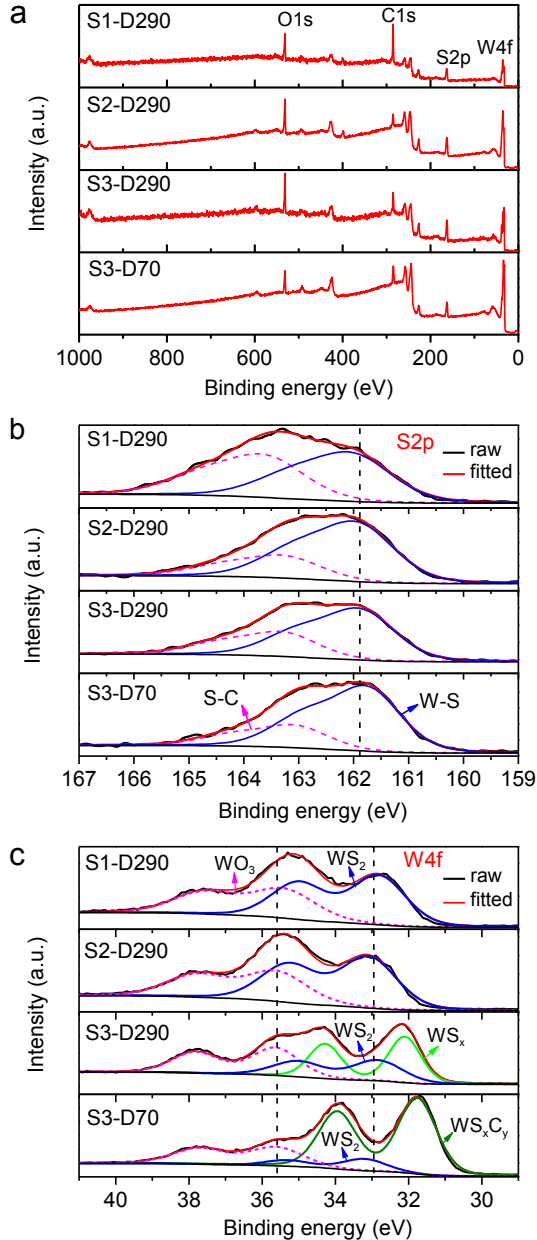
around  $2\theta = 33^\circ$  with a long tail. This is generally ascribed to the effect of the turbostratic stacking of  $WS_2$  basal planes with other planes. Weise *et al.*[27] reported that the referred XRD patterns of TMD point to a two-dimensional (2D) organization of the basal planes with several tens of unit cells. The stacking in the c-direction of the a-b basal lattice planes with lateral dimensions in the range of a few nanometers, results in a sharp peak at approximately the position for the (100) reflections. The peak tails towards larger angles suggesting other reflections of the (10Z) family with  $Z = 1, 2, 3...$ [27,31] and consequently presenting broader peaks typically of an amorphous structure.

Since the most important diffraction pattern of (002) basal plane is usually absent in the reported XRD spectra of TMDs [36–39], it is crucial to mention that provided the target-substrate distance is beyond 145 mm, a (002) peak of  $WS_2$  was detected in S3 coatings. The comparisons of  $WS_xC$  with a pure sputtered  $WS_2$  coating (see Ref. [32]) evidences a slight shift of the (002) peak towards lower diffraction angles from ( $\sim 14^\circ$  to  $12^\circ$ ) when  $WS_2$  is doped with carbon because carbon incorporation increases the lattice parameters of  $WS_2$  [37]. A similar lattice expansion was also reported in Ti- $WS_2$  coatings [40]. The strong (002) reflection indicates that some  $WS_2$  crystals are oriented with basal planes parallel to the surface, which is typical for a type II structure of sputtered TMD coatings [1]. The basal plane orientation of  $WS_2$  plays a vital role in various applications including tribo-fields (minimum friction, strong adhesion to substrate and inertness to oxidations) [41] and even in thin film solar cells (high absorption coefficient) [23]. Numerous strategies such as pressure control [32], doping with Ni [12], deposition temperature [23] and different atmospheres [26] were exploited to realize films with well aligned basal planes. This study indicates that a larger target-substrate distance may offer an alternative route to achieve the desired orientation of the basal planes in  $WS_2$  films. Besides, Cr diffraction peaks arise from the interlayer (see **Figure 4.4a** and **b**).

The chemical bonds of the  $WS_xC(H)$  composite coatings deposited at  $D = 290$  mm were characterized by XPS spectra, as shown in **Figure 4.5**. As an example, S3-D70 coating was also analyzed for comparisons. To avoid possible sputter damages such as sulfur resputtering and chemical state variations [42], no preliminary Ar etching process on as-deposited coatings was applied. **Figure 4.5a** shows the survey scans, where the W4f, S2p, C1s and O1s peaks are evident for all coatings. However, the intensity of the C1s peak is more prominent in coating S1-D290, while the O1s peak is less intense in coating S3-D70, in agreement with the EDS data discussed earlier.

The C1s peaks at a binding energy (BE) of 284.5 eV [43] corresponds to amorphous carbon. The detailed S2p and W4f spectra are shown in **Figure 4.5b** and **c**. The S2p doublets with maxima at 161.8 eV and about 163.6 eV correspond to S-W and S-C bonds [34,37,43,44]; the latter are probably located at the interface between the  $WS_2$

and the amorphous carbon. In particular, the intensity of S-C bonds contributes as much as 46.7% to the total S signal for the high-carbon coating S1-D290.



**Figure 4.5** XPS spectra of the coatings deposited at various conditions: (a) survey scan; (b) high resolution scan of  $C1s$  spectra; (2) high resolution scan of  $S2p$  spectra; (3) high resolution scan of  $W4f$  spectra. Note that the spectra are the averaged value of three measurements for each test.

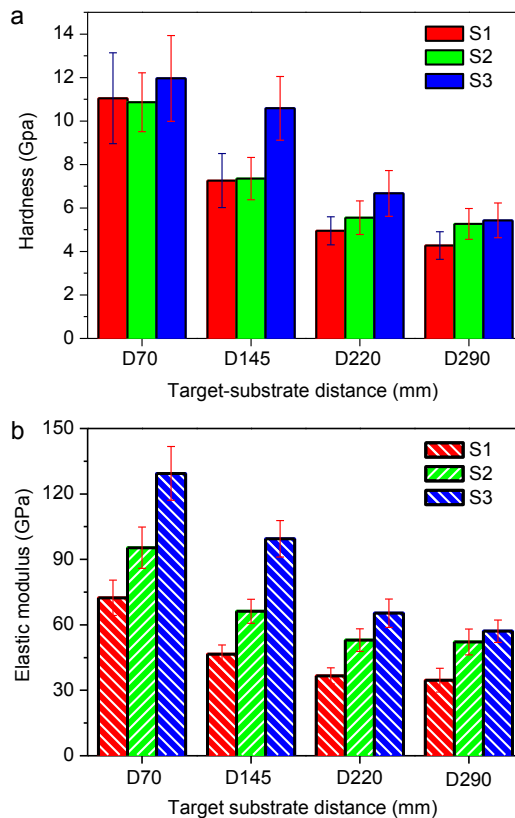
The deconvolution of the W4f7/2 spectra (**Figure 4.5c**) demonstrates the presence of W-S and W-O bonds at BEs of 32.9 eV and 35.6 eV, respectively, which can be ascribed to WS<sub>2</sub> and WO<sub>3</sub> [37,42,43,45]. The third W4f7/2 contribution situated at a BE of around 32.1 eV [37] present for the coating S3-D290 is attributed to WS<sub>x</sub> (x < 2). Another lower BE component at 31.7 eV in the spectrum of the coating S3-D70 stems from W-C bonds [37,43,45]. Coatings S3-(D70, D290) should have close chemical state since they are both deposited by cosputtering, thus WC in coating S3-D70 is supposed to mingle with WS<sub>x</sub> and it is probably more suitable to ascribe this component to an intermediate mixture of WS<sub>x</sub>C<sub>y</sub>, similar to the reported TiS<sub>x</sub>C<sub>y</sub> [37]. In addition, Ar<sup>+</sup> bombardment can induce reduction of W in high valence states [45,46], e.g. W(6<sup>+</sup>) to W(0) and the sulfur preferential lost from the surface also enriches the surface in metallic W. The coating S3-D70, produced under the strongest Ar<sup>+</sup> bombardment, is highly rich in tungsten (47.3 at.%), so the low-BE component at 31.4 eV [45,47] presumably contains a contribution from metallic W. This is also supported by a broader FWHM of 1.2 eV as compared to 1.0 eV for coating S3-D290. However, it is difficult to separate the contribution of WC from that of metallic W because their BEs are close. Note that WO<sub>3</sub> may mainly arise from surface oxides since W-O bonds can be remarkably reduced after ion sputter etching [37,42,45]. This can be reconfirmed by the lowest WO<sub>3</sub> contribution in the coating S3-D70: the heavy bombardment under which this coating was produced, diminishes the number of active sites for oxidization at the expense of a sufficient amount of S (S/W = 0.51). Although no clear W-C peaks are detected in the XRD (see **Figure 4.4**), we cannot rule out the possibility that WC is amorphous and randomly distributed in the matrix [37,44].

### 4.3.2 Mechanical properties

Figure 4.6 shows the average hardness (H) and elastic modulus (E) of all the WS<sub>x</sub>C(H) coatings. First, a significant decrease in hardness was observed with increasing target-substrate distance from 70 to 220 mm but then remains nearly unchanged on going from 220 to 290 mm. The nonreactive coating was found to have an overall higher hardness, from ~ 12.0 GPa at D = 70 mm to 5.4 GPa at D = 290 mm. The hardness of S1 and S2 coatings showed a similar trend with a decrease from 11.0 GPa to 4.3 GPa. It should be pointed out that compared with the pure sputtered WS<sub>2</sub> coatings with hardness < 1 GPa [18,32], above one order of magnitude higher hardness can be attained by the incorporation of moderate amounts of carbon into WS<sub>2</sub>. Carbon addition enhances the compactness of the coating and facilitates possible formation of strong W-C bonds as discussed for the XPS results of coating S3-D70 [37]. Our earlier results [32] showed that the hardness of WS<sub>2</sub>/a-C coating increases with increasing carbon content up to ~ 40 at.%, reaching a maximum of 10.6 GPa, but then levels out or even decreases upon further higher carbon content. As discussed in Figure 1a, S1 has a relatively high carbon content as compared to S2 and S3 (~ 70 at.% vs. 20 at.%), but its hardness is even slightly lower than that of the latter. In fact, these major

hardness variations can again be explained by the effect of Ar bombardment: the S3 coatings were deposited a pure Ar atmosphere with the highest flux (25 sccm) yielding the strongest bombardment with energetic particles. This indirectly explains why coatings deposited at shorter target-substrate distances present a higher hardness. The decreased Ar flow rate from 20 sccm (S2) to 15 sccm (S1) reduces the hardness.

The variations in elastic moduli, shown in **Figure 4.6b**, closely track the hardness variations, with the highest elastic modulus of 129.4 GPa measured for coating S3-D70 and the lowest of only 34.6 GPa for coating S1-D290. According to the Leyland's findings [48], high H/E ratio is commonly regarded as a reliable indicator of better wear resistance for DLC-based coatings. The H/E ratio of the WS<sub>x</sub>C(H) coatings tends to decrease with increasing target-substrate distance for S1 and S2. For instance, the H/E of S1 coatings equals to 0.15, 0.16, 0.13 and 0.12 respectively, as the target-substrate distance increases from 70 mm to 290 mm. While the H/E ratio for S1 is slightly higher than S2, S3 almost has the same H/E values of ~ 0.1. To conclude, a shorter target-substrate distance leads to microstructure densification, which potentially enhances the wear resistance.



**Figure 4.6** (a) Hardness and (b) elastic modulus of all tested coatings.

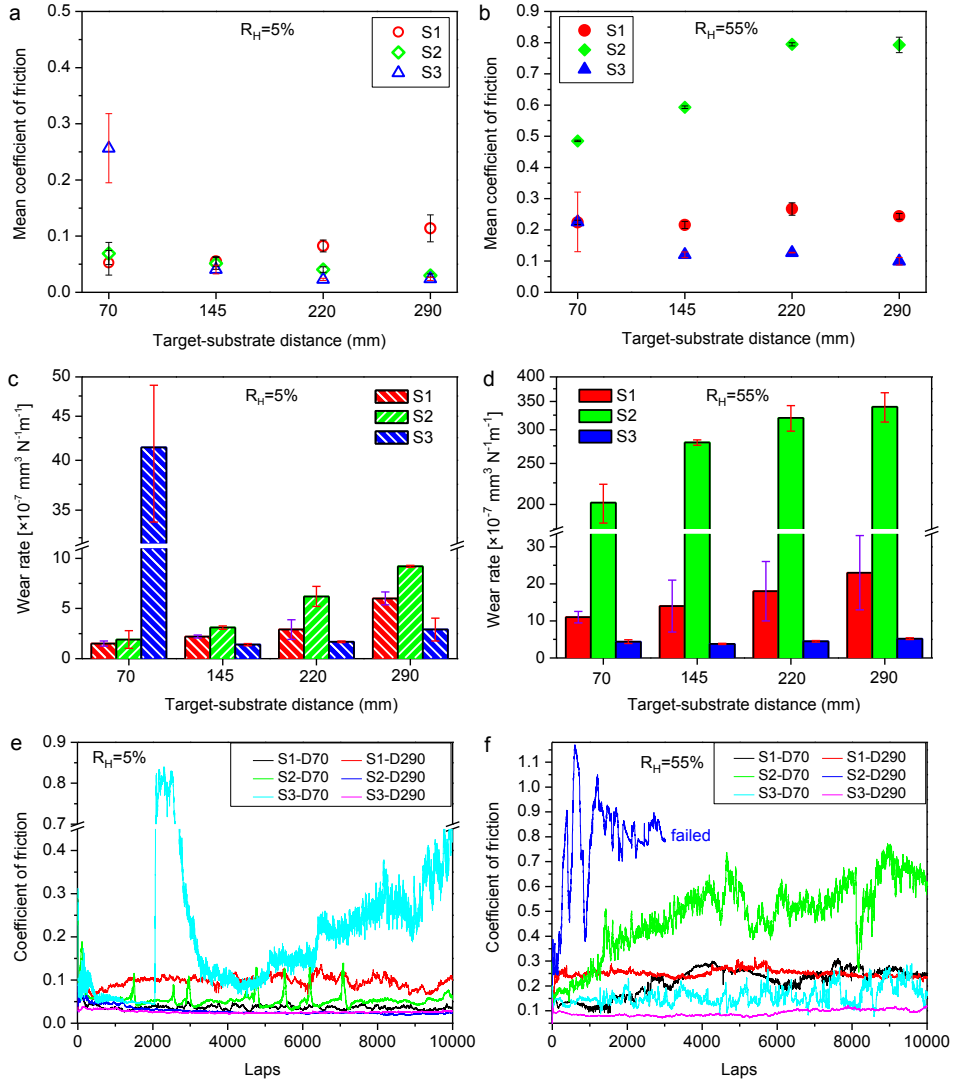
### 4.3.3 Tribological properties

Pin-on-disk wear tests were performed under dry air (5%  $R_H$ ) and humid air (55 %  $R_H$ ). **Figure 4.7a** and **b** show the mean CoF for all the tribotests over 10000 sliding laps, whereas **Figure 4.7c** and **d** show the wear rate. **Figure 4.7e** and **f** display the instant CoFs of the coatings deposited at a target-substrate distance of 70 mm and 290 mm, respectively. **Figure 4.8** presents the morphologies of wear tracks and corresponding counterpart scars. For sliding in dry air, the behavior of coating S3-D70 showing a high CoF of  $0.26 \pm 0.08$  with large deviations, is remarkably different from that of the other coatings which exhibit relatively low CoFs. In particular, minimum values of  $0.023 \pm 0.02$  and  $0.024 \pm 0.02$  are measured for the coating S3-D220 and S3-D290. In fact, CoFs of the coatings S2 and S3 with similar content of carbon (~ 20 at.%) slightly decrease with higher S/W ratio that results at larger target-substrate distance. On the contrary, the CoFs of high-carbon S1 coatings present an upward trend with target-substrate distance, with a lowest value of 0.053 for the coating produced at  $D = 70$  mm and the highest CoF of 0.114 for the one deposited at  $D = 290$  mm. The wear rates,  $W_R$ , are depicted in **Figure 4.7c**. A strikingly high  $W_R$  of  $4.14 \times 10^{-6} \text{ mm}^3\text{N}^{-1}\text{m}^{-1}$  stands out for coating S3-D70, while the wear rates of the other coatings are all one order of magnitude lower, reaching down to a  $W_R$  of  $1.4 \times 10^{-7} \text{ mm}^3\text{N}^{-1}\text{m}^{-1}$  for coating S3-D145. In general,  $W_R$  increases with increasing target-substrate distance. Overall the higher H/E ratio may account for the lower  $W_R$  of S1 as compared to S2, considering that both are hydrogenated coatings with comparable hardness, as indicated in **Figure 4.6a**.

For tribotests in humid air of 55%  $R_H$ , the CoFs of the cosputtered S3 coatings are much lower than those of the reactively sputtered S1 and S2 coatings. The CoFs of S3 coatings in humid air remain in the range of 0.10-0.13 - except for S3-D70, where its CoF reaches 0.023, while the CoFs of high-carbon coatings S1 range between 0.22 and 0.27. The CoFs of S2 coatings are surprisingly high, increasing from 0.48 to 0.80 with increasing target-substrate distance. This reveals a coating failure as a  $\text{CoF} > 0.6$  is usually regarded as an indicator of direct metal contact [49]. This deterioration is confirmed by the high  $W_R$  coming into the range of  $10^{-5} \text{ mm}^3\text{N}^{-1}\text{m}^{-1}$  as shown in **Figure 4.7d**. Similarly, the  $W_R$  of S1 coatings increases from  $1.1 \times 10^{-6} \text{ mm}^3\text{N}^{-1}\text{m}^{-1}$  to  $2.3 \times 10^{-6} \text{ mm}^3\text{N}^{-1}\text{m}^{-1}$ , which is still higher than that of S3 coatings where the wear rate remain in the range  $3.8\text{-}5.2 \times 10^{-7} \text{ mm}^3\text{N}^{-1}\text{m}^{-1}$ .

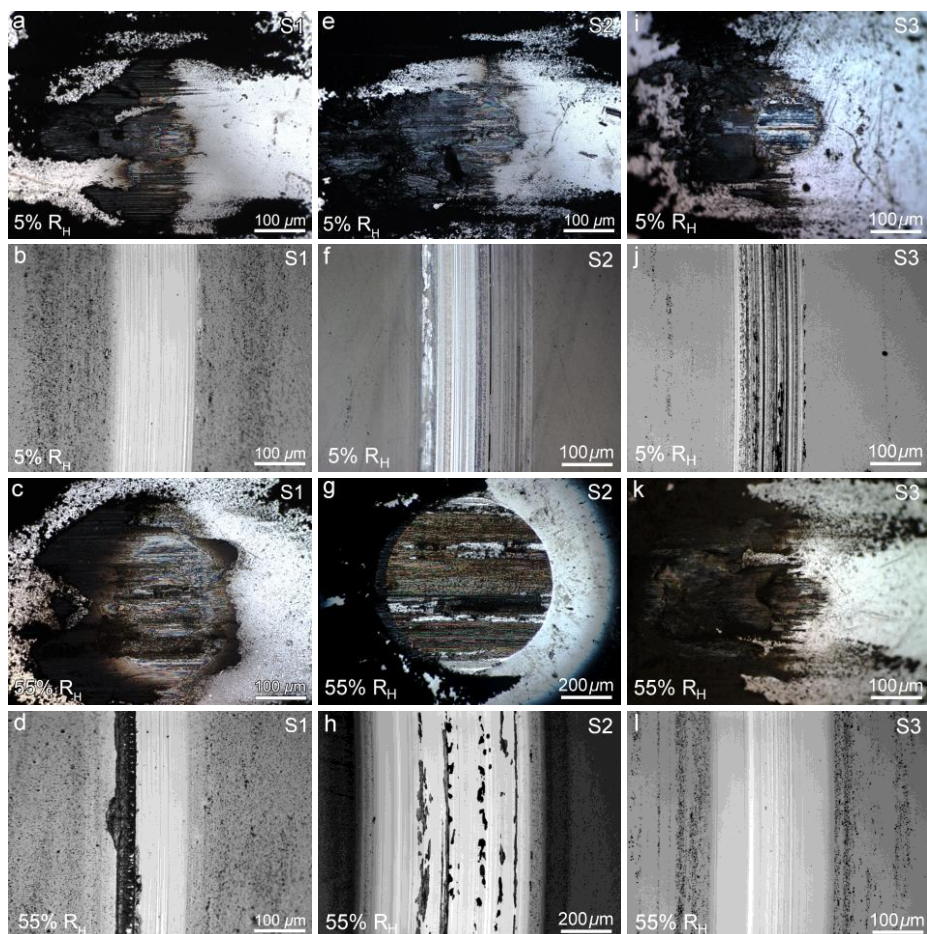
A closer look at **Figure 4.7e** reveals that for coating S3-D70, the CoF in dry air shows great fluctuations. In fact it starts from 0.4 and decreases to 0.05 after sliding 1000 laps; after sliding for 2000 laps the CoF increases to 0.8, followed by leveling off at about 0.1 and rebounding to 0.4 at 10000 laps ultimately. In contrast, S3-D290 exhibits an initial ultralow CoF of 0.026, which remains rather constant (0.02) during the entire test and the same coating tested in humid air has a CoF which stabilizes rapidly at 0.10 (see **Figure 4.7f**). (S1, S2)-D290 respond instead much more negatively to the presence of humidity. An immediate rise of CoF to 1.1 manifests an rapid catastrophic failure for

S2-D290 in humid air. **Figure 4.8** (a, b, e, f, i, j) confirm comparable wear scar/track widths ( $\sim 140 \mu\text{m}$ ) of all coatings in dry sliding. The transfer layers densely cover the whole wear scars and leave debris behind. Substantial adhesive tribolayers are formed in the wear track of the S3-D290 (see the dark areas in **Figure 4.8j**). While only S3-D290 coating survives intact in humid air, S1-D290 suffers from partial coating delaminations (see **Figure 4.8d**) and the huge wear width up to  $750 \mu\text{m}$  (see **Figures 4.8g** and **h**) confirms a total failure for coating S2-D290.



**Figure 4.7** Coefficient of friction (CoF) and wear rate of  $WS_xC(H)$  coatings under different target-substrate distances: (a, b) average CoF; (c, d) Wr; (e, f) typical CoFs of coatings deposited at  $D = 70$  and  $D = 290$  mm, respectively (5N load).



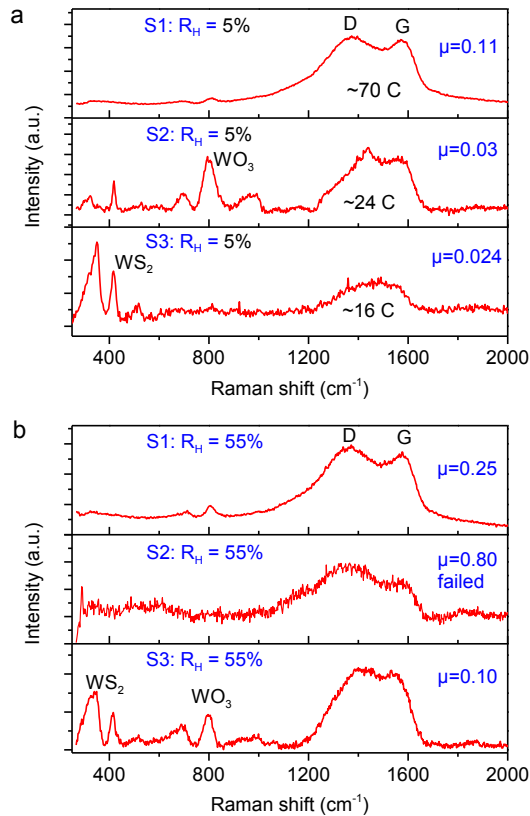


**Figure 4.8** Optical micrographs of wear scars of 100 Cr6 steel ball counterpart and wear tracks of  $WS_xC(H)$  coatings ( $D = 290$  mm) tested in dry air ( $R_H = 5\%$ ) and humid air ( $R_H = 55\%$ ): (a-d) S1-D290; (e-h) S2-D290; (i-l) S3-D290.

It can be concluded that no matter whether in dry or humid air, the S3 coatings outperform the S1 and S2 coatings in terms of low CoF and  $W_R$ , provided that they were produced at target-substrate distances above 145 mm. This indicates intrinsically different lubrication mechanisms for the  $WS_xC(H)$  nanocomposite coatings with varied S content. The triboperformance is also influenced by the type of sputtering process used to fabricate the coating. Hydrogenated and non-hydrogenated DLC-based coatings tribologically behave differently in that hydrogenated coatings exhibit ultralow friction in dry air while the non-hydrogenated coatings perform better in humid atmosphere [50].

**Figure 4.9** shows the Raman spectra on the wear tracks of the coatings deposited at  $D = 290$  mm. For dry air sliding, **Figure 4.9a** indicates the high-carbon S1 coating (70.0

at.% C) shows Raman-active bands exclusively in the 1300-1600  $cm^{-1}$  region, corresponding to the typical D ( $\sim 1360\text{ cm}^{-1}$ ) and G ( $\sim 1565\text{ cm}^{-1}$ ) peaks of amorphous carbon; this indicates that the hydrogenated DLC matrix contributes a low-friction tribological behavior. The  $WS_2$  peaks  $E_{12g}$  ( $\sim 355\text{ cm}^{-1}$ ) and  $A_{1g}$  ( $\sim 421\text{ cm}^{-1}$ ) characteristic of hexagonal  $WS_2$  [40] appear in coating S2-D290. For this coating, the significant reduction of CoF from 0.11 to 0.03 at the onset of sliding suggests that  $WS_2$  starts to perform. This can be further confirmed by the Raman spectrum of the S-richer S3 coating (51.8 at.% S) where a high intensity of  $WS_2$  appears and an ultralow CoF (0.024). Such an ultralow CoF is rarely reported for the nonhydrogenated DLC in dry air, which normally has a CoF above 0.1 before graphitization [6]. The ultralow CoF is thus predominantly attributed to the lubricating effect of the  $WS_2$  phase.



**Figure 4.9** Raman spectra of the wear tracks of  $WS_xC(H)$  coatings deposited at  $D = 290\text{ mm}$  after sliding for 10000 laps in different humidities: (a)  $R_H = 5\%$  and (b)  $R_H = 55\%$ .

**Figure 4.9b** shows that only the D and G bands were measured on the wear tracks of S1-D290 pointing to the fact that the CoF of 0.25, a value commonly measured for the hydrogenated DLC in humid air, is primarily determined by the DLC matrix [50]. Note

that for the S2 coating where, as discussed previously (**Figure 4.7f** and **Figure 4.8g** and **h**), catastrophic failure occurred, the weak D and G peaks and the small signal from WS<sub>2</sub> in the Raman spectrum in **Figure 4.9b** probably arise from the very thin residual film on the damaged wear tracks (see **Figure 4.8h**). The S3-D290 coating, whose low CoF of ~ 0.10 in humid air was attributed to both DLC and richness in WS<sub>2</sub>, shows a Raman fingerprint with stretching bonds of WO<sub>3</sub> at 700-810 cm<sup>-1</sup>[19] testifying to oxidation. The latter was probably produced mostly by reactions of WS<sub>2</sub> with H<sub>2</sub>O from the humid air. Previous results [51] have suggested that only absorbed water attacks dangling bonds at WS<sub>2</sub> edge sites or defects, leading to larger lamellar attractions and thus higher shear strength. Correspondingly a higher CoF results and thus thicker debris covering the ball as seen in **Figure 4.8k** if compared to **Figure 4.8i** which depicts the dry sliding wear track.

There are contrasting results reported in the literature concerning the origin of the triboperformance of WS<sub>2</sub>/a-C coating; in fact Voevodin and coworkers assign the chameleon behavior of this coating to the joint contribution of DLC and WS<sub>2</sub> [15,16], but recent results presented by Polcar et al. [38,52] suggested that only WS<sub>2</sub> phases provide lubrication whereas carbon improves the overall mechanical properties. This suggests a potential contribution of DLC matrix in reducing CoF and in increasing the wear resistance. Indeed, although the presence of amorphous carbon in all wear tracks is confirmed by the Raman spectra, the (S2, S3)-D290 coatings of approximately same hardness and elastic modulus behave differently in tribo-performance, particularly in humid air (CoF: 0.8 vs. 0.10, and W<sub>R</sub>: 10<sup>-5</sup> mm<sup>3</sup>N<sup>-1</sup>m<sup>-1</sup> vs. 10<sup>-7</sup> mm<sup>3</sup>N<sup>-1</sup>m<sup>-1</sup>). The lubrication of WS<sub>2</sub> in (S2, S3)-D290 coatings is comparable considering that their chemical composition is very similar (see **Figure 1a**). This implies that the unhydrogenated DLC matrix at least partially plays a role as lubricant in humid air sliding. Earlier work [32] also reported C-rich WS<sub>2</sub>/a-C coating presents much lower W<sub>R</sub> in humid air sliding. However, further pertinent experiments and MD simulations are required to unravel the underlying mechanism for this behavior.

Notably, to achieve an ultralow friction it is not necessary to reach the stoichiometric WS<sub>2</sub> in the WS<sub>x</sub>C(H) coatings. A clear correlation can be found between the S/W ratio (**Figure 1b**) and the CoF (**Figure 4.7a** and **b**), displaying values below 0.05 (in dry air) and 0.10 (in ambient air) for ratios S/W ≥ 0.95, provided the target-substrate distance exceeds 145 mm. A threshold value of Se/W ≥ 0.6 was also found in WSeC to be sufficient to reduce the CoF below 0.1 even in ambient air and no further reduction occurred for Se/W > 1 [39]. Our earlier work [32] demonstrated stable ultralow CoFs in the level of 0.02, almost independently of the S/W ratio in the range S/W = 1.33-1.79. Yet contrasting with Ref. [53], where MoS<sub>2</sub>/a-C coatings with low sulfur content (< 10 at. %) and ultralow(Mo+S)/C ratio (0.04-0.19) could produce low CoFs in diverse environments (air, N<sub>2</sub>, vacuum), this study indicates that besides the appropriate S/W ratio, a high total content of sulfur is equally crucial for an ultralow

friction. For S1 coatings, all with < 20 at. % S content, show a higher CoF as compared to S2 coatings when sliding in dry air. Particularly for the W-rich S3-D70 coating, both the low S/W ratio (0.51) and low S total content result in unacceptable triboperformance (see **Figure 4.7**). The low sulfur content makes it more difficult to reorient WS<sub>2</sub> platelets parallel to the wear interface or entails longer sliding time to do so [32]. Ref. [32] also reported a worse triboperformance for the S-poor WS<sub>x</sub>C coating with a high S/W ratio (1.79). These results agree with the findings by Voevodin et al. [6] that WS<sub>x</sub>C coatings with scarce sulfur content perform unsatisfactorily in dry conditions. It can be concluded that, for tribological applications, WS<sub>x</sub>C(H) coatings are not necessarily to reach WS<sub>2</sub> stoichiometry by excessively increasing the target-substrate distance, which potentially undermines the wear resistance due to significant reduction in hardness and compactness and also lowers the deposition rate (see **Figure 4.3**).

## 4.4 CONCLUSIONS

WS<sub>x</sub>C(H) nanocomposite coatings were prepared either by reactive sputtering or nonreactive co-sputtering. This work mainly studied the effect of the target-substrate distance on the S/W stoichiometry, the microstructure and the structure-property relationship. The lubricating mechanisms were also discussed.

- For WS<sub>x</sub>C(H) nanocomposite coatings, the S/W stoichiometric ratio increases with target-substrate distance. Randomly-oriented WS<sub>2</sub> platelets are observed in the co-sputtered S3-D290 coating. Preferential resputtering of sulphur reinforced by energetic particles impingement on the growing coating primarily accounts for the low S/W ratio.
- The hardness and elastic modulus decrease with increasing distance between target and substrate and the co-sputtered S3 coatings show overall a higher hardness and larger elastic modulus than the reactively sputtered S1 and S2 coatings.
- For dry air sliding (< 5% RH), low CoFs could be reached in all WS<sub>x</sub>C(H) coatings except for coating S1-D70 characterized by both low S/W ratio and low S content. Co-sputtered WS<sub>x</sub>C coatings are preferable for tribological applications in high humidity.

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