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The Influence of Substrate Bias on the Mechanical Properties of a W- and S-containing DLC-based Solid-lubricant Film

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Abstract**—**A diamond-like carbon (DLC) based solid-lubricant film was designed and DLC films were successfully prepared using a microwave plasma enhanced magnetron sputtering deposition technology. Post-test characterizations including Raman spectrometry, X-ray diffraction, nano-indentation test, adhesion test, friction coefficient test were performed to study the influence of substrate bias voltage on the mechanical properties of the W- and S-doped DLC films. The results indicated that the W- and S-doped DLC films also had the typical structure of DLC films and a better mechanical performance achieved by the application of a substrate bias of -200V.

Keywords**—**Adhesive Strength, Coefficient of Friction, Substrate Bias, W- and S-doped DLC film

I. INTRODUCTION

MULTIFUNCTIONAL composite DLC films have continuously been promising in the past decades because of the special properties, such as good chemistry-stability and outstanding mechanical and physical properties [1], [2], in which, the low friction and high hardness qualify such films as an alternative to solid lubricants [3], [4]. Meanwhile, considerable attention has been paid to the development of existing lubricant films by multilayer, composite film or ion beam assistance [5].

It is well-recognized that adding different elements to DLC films leads to improvement of some properties for specific applications. For instance, doping of N or F element into the films can improve their hydrophobic property [6], while S element and metal additions have the potential to modify the tribological behavior under various working conditions [7], [8]. In this paper, W and S elements were incorporated into the DLC matrix aiming to further improve the tribological and wear behavior. The influence of substrate bias on the mechanical properties of W- and S-containing DLC films was investigated.

II. EXPERIMENTAL DETAILS

A three-target (Φ120mm) magnetron sputtering system was used in this study including a graphite target, a tungsten target and a tungsten sulfide target.

A detailed description of the deposition system can be found in Ref [9]. The distance of the targets and substrate all is 115 mm. All bearing steel samples were first burnished and polished, followed by ultrasonic cleaning in ethanol, finally installed onto the holder in the deposition chamber. Prior to coatings deposition, Ar ion sputtering clean was processed for 30 min when the background pressure was in 6×10^{-2} Pa to remove undesirable contamination layers. Then a tungsten transition-layer was first deposited onto the substrate for about 15 min at the working pressure of 0.1 Pa. After that the composite layer was deposited with all three targets sputtering together for about 50 min at the working pressure of 0.2 Pa. The transition-layer and the composite layer formed are about 300nm, 800nm, respectively. In all experiments, microwave ECR plasma discharge system was operated with 360 W microwave power and 64 A magnetic coil current to strengthen plasma density. Four different samples were fabricated by changing the substrate voltage when the other parameters are fixed. The voltages are -100V, -200V, -300V, -350V, respectively, and other parameters were listed in table I.

The chemical composition and bonding of the films were analyzed using Raman spectroscopy and X-ray diffraction. The adhesion of the films was estimated using a WS-2004 scratch tester with a diamond tip at a load rate of 100 N/min and a constant sliding speed of 8.0 mm/min. Three scratches were made on each sample to avoid testing anomalies. The nano-hardness and elastic modulus of the films was investigated by a Nano-Indenter with continuous stiffness measurement. The nominal load was set to be 1 mN assuming a Poisson ratio of 0.3. Coefficient of friction (CoF) of the films was evaluated by Universal Micro-Tribometer (UMT) with a vertical nominal load of 0.5 N applied by a 4-mm-diameter GCr15 ball at a room temperature of 25 ℃ and a relative humidity of 30%. Reciprocating speed was set to be 240 cycles per minute with the reciprocating displacement of 7 mm, corresponding to a speed of 28 mm/s.

TABLE I
THE PARAMETERS OF A W- AND S-CONTAINING DLC FILM S

	Transition- Layer	W- and S-containing DLC Layer
Gas Flow Rate(cm^3/s)	$Q_{Ar}=10$	$Q_{Ar}=12$, $Q_{H2}=6$
Sputtering Target Power (W/cm^2)	$P_W=5.3$	$P_W=3.97$, $P_C=5.8$, $P_{WS2}=5.2$
Sputtering Target Current (A)	$I_W=1.5$	$I_W=1$, $I_C=1.2$, $I_{WS2}=1$
Substrate Bias (V)	-100	-100, -200, -300, -350

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III. RESULTS AND DISCUSSION

A. Chemical Bond and Composition

The Raman spectrum of hydrogenated amorphous carbon (a-C:H) film is dominated by two features, a D peak around 1355 cm^{-1} and a G peak at around 1575 cm^{-1}. G peak is corresponding to all sp^2 bonds and D peak is only corresponding to loop structures of sp^2 bond. As shown in Fig.1 (a), the W- and S-doped DLC films also have the typical structure of DLC films with the fitting Gauss peaks of D (at approx. 1380 cm^{-1}) and G (at approx. 1580 cm^{-1}). More generally, the sp^2 cluster size and the sp^3 content are identified by the I(D)/I(G) area ratio of the two peaks and the center position ω_G of the G peak [10,11]. With the sp^3 content increasing, the I(D)/I(G) value of the film will decrease and G peak will shift to low wavenumber. As shown in Fig.1 (b), with negative bias increasing, G peak position moved up to high wavenumber and the I(D)/I(G) value of the samples gradually increased. Based on the above results and discussion [12], it is believed that the sp^3 content of the samples also gradually decreased with the bias increasing. This phenomenon was attributed to sp^3 decomposition and sp^2 hybridization (graphite-like) made by the excessive ion bombardment as increasing bias voltage.

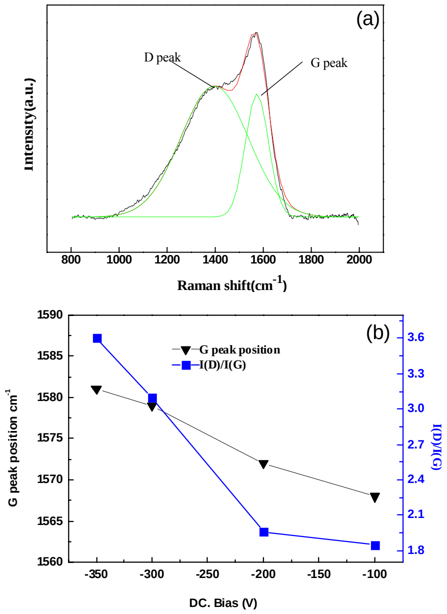

Fig. 1 Raman spectra of W- and S-doped DLC film. (a) Raman spectra of W- and S-doped DLC film at -300V. (b) G peak position and *I(D)/I(G)* ratio versus bias

The XRD curves of four samples were shown in Fig.2. The diffraction peaks are mainly composed of WC, W and WS_2. It was found that the intensity of WC peak gradually strengthened with the substrate bias increasing, while the WS_2 peak gradually decreased or even disappeared. For example, the XRD curve of the sample at -350 V lacked two WS_2 peaks and has very weak WS_2 peaks, as compared with the sample at -100V. The reasons could be attributed to strong ion bombardment effects, which could lead the substrate temperature into increment and cause some chemical bond to compose and decompose, accordingly in the film stable WC phase gradually increasing and instable WS_2 phase gradually reducing with the substrate bias increasing. Combined with the results from Raman spectrometry, the W- and S-containing particles were affirmed, which indicated the composite DLC films were consisted of DLC matrix, W- and S-containing particles.

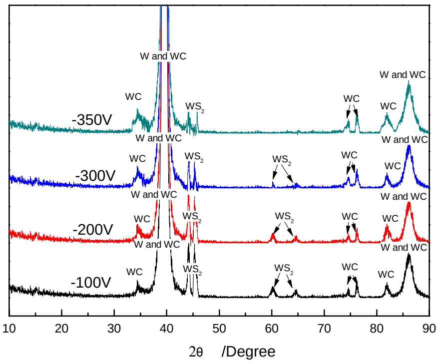

Fig. 2 The XRD spectrum of W- and S-doped DLC films at different bias

B. Mechanical Properties

Both nano-hardness and elastic modulus of the W- and S-doped DLC films increase and then reduce with the increasing DC bias, and the highest values of hardness and elastic modulus are obtained at the bias of -200V, as shown in Fig.3. Actually, the main influential factors in the hardness and modulus of the film are its chemical bond and composition, such as sp^3, sp^2 and WC content. The graphitization transformation concomitant with the increasing of ion energy actually is responsible for the reduction of the hard phase of sp^3[13].When the substrate bias is -200V , the sp^3 content of the film is yet more and WC content is increased, so the hardness and modulus of the film is increased. When the substrate bias increases to -300V and -350V, the sp^3 content of the film significantly reduced and WC content is obviously increased, but it still can't make up for the hardness loss of the sp^3 content decreasing, so the hardness and modulus drop sharply.

Fig.4 shows that the adhesive strength of W- and S-doped DLC films estimated using a microscratch testing. In order to evaluate the film adhesion, microscratch testing was conducted using friction force sensor as an intensity signal gathering unit. By ramping the indenting load at the range from 0 N to 100 N, followed by observing curve variation and visual examination of the scratch, the critical load which just causes adhesion failure can be determined. When the indenting load is beyond the critical load, the strong fluctuation of the curve will be produced, which indicates the film has birthed adhesion failure. As evidenced in Fig.4, the adhesive strength of the DLC films significantly enhanced by W doping and all samples' critical load are over 75N, especially the samples at -100V and -200V, whose critical loads reach about 100N.

But, with the bias increasing, the critical load of the sample gradually decreased due to intrinsic stresses induced by ion bombardment. The result provided evidence that the W doping, proper ion bombardment and transition-layer could enhance the adhesive strength due to alleviating internal stress in the DLC film and the dismatch influence of thermal expansion coefficient of the DLC film and substrate.

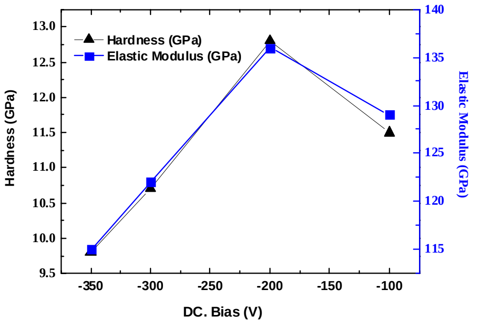

Fig. 3 The hardness and elastic modulus of W- and S-doped DLC films as a function of substrate bias

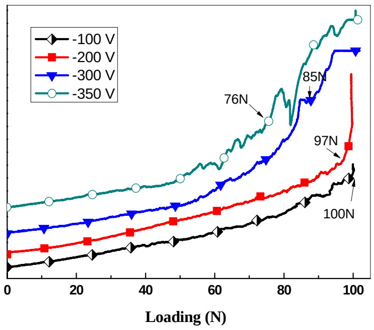

Fig. 4 The adhesive properties of W- and S-doped DLC films at different bias

Typical CoF-time curves of W- and S-doped DLC films at different bias were illustrated in Fig. 5. Fig. 5 (a) shows that the CoF-curve of the sample at -200V, the friction behavior in air became unstable after W and S element doping, requiring a longer accommodationm stage up to almost 1600 cycles. Fig.5 (b) shows that the CoF-curve of the sample at -350V, which produced stronger oscillation. As exhibited in Fig. 5 (c), the steady state CoF decreases and then increases with the increasing DC bias and the lowest coefficient of friction is about 0.04 after 8400 cycles of testing when the applied bias is -200 V. The value is lower, than that of a carbon- tungsten-sulfur film system obtained by J.H. Wu et al [14]. The influence factor on the CoF of the doped DLC film could be attributed to the hardness and the composition of the film, such as the content of WC, WS_2 and sp^3 in the case. When the substrate bias is at -200V, the film has higher hardness and WS_2 and sp^2 self-lubricant, so the CoF of the film is lowest in these samples. When the substrate bias continues to mount up, the sp^3 of the film produces graphitizing, the hardness of the film becomes soft, large WC particles increases, and the WS_2 lubricant phase decomposes, which results in the increasing of the film's CoF.

The frictional mechanism of W- and S-doped DLC films is complex, which can be divided into the following points. Firstly, the big particles formed in the films such as W and W_xC could cause a long unstable stage and the bigger changing of CoF at the beginning in the frictional testing. Secondly, during friction processes, the release of hydrogen in DLC film caused lattice relaxations, and then shear deformation promotes a graphitic structure at the surface. Thirdly, for W- and S-doped DLC film, WS_2 could form a sandwich interlayer structure (S-W-S), which is loosely bound to each other only by van der Waals forces [15]. This weak bonded layered structure can provide a similar lubrication with the sheet structure in graphite.

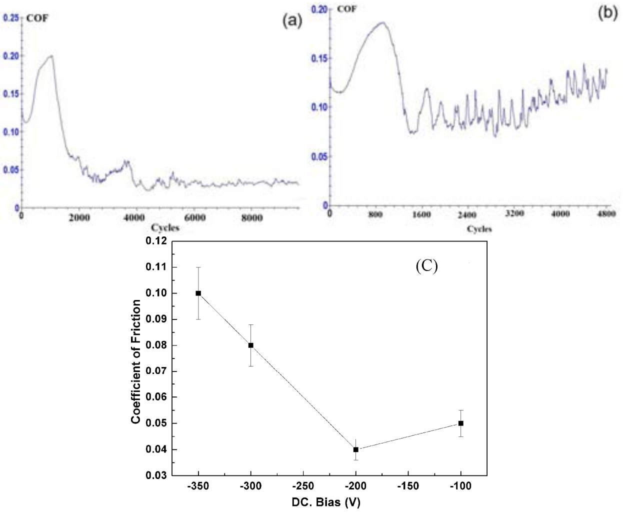

Fig.5 The CoF of W- and S-doped DLC film at different bias. (a) CoF curve of W- and S-doped DLC film at -200V. (b) CoF curve of W- and S-doped DLC film at -350V. (c) The CoF of W- and S-doped DLC film as a function of substrate bias

IV. CONCLUSION

W- and S-doped DLC-based solid-lubricant films were designed and successfully prepared using magnetron sputtering deposition technology. The substrate bias was adjusted to investigate its influence on the mechanical properties of the W- and S-doped DLC films. The results indicated that the substrate bias had a considerable influence on the chemical composition and the mechanical properties of the solid-lubricant film. With the increasing of substrate bias, the sp^3 bond and WS_2 phase in the film gradually decomposed, hard WC content increased, and the doped films became more graphite-like, so some properties of the film became degraded. But at the substrate bias of -200V, an excellent mechanical performance (hardness, elastic modulus, adhesion and friction) was achieved.

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