

Effect of substrate bias on microstructure and tribological performance of GLC films using hybrid HIPIMS technique

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Abstract: The Cr-doped hydrogen-GLC films were prepared by a hybrid magnetron sputtering system composed of a direct current magnetron sputtering (DC-MS) source of carbon and a high power impulse magnetron sputtering (HIPIMS) source of Cr with reactive gas of C₂H₂. The hydrogen-free GLC and Cr-doped GLC films were also prepared for comparison. The influence of substrate bias on the Cr-doped hydrogen-GLC films was investigated. With the increase of substrate bias from -100 V to -250 V, the re-sputtering of weak bonding sp² firstly occurred and induced an increased sp³ bonding. However, the following sp³ to sp² transformation resulted in a decreased sp³ bonding. The change trends of surface roughness and friction coefficient with the increased bias voltages were the same as those of sp³ bond. The lowest surface roughness and lowest friction coefficient corresponded to the highest sp³ with the Cr-GLC-H films at the bias voltage of -100 V.

Key words: graphite-like carbon; high power impulse magnetron sputtering; substrate bias; microstructure; tribological behavior

1 Introduction

Carbon is one of the most remarkable elements among all others in the periodic table. It has the largest number of allotropes and can exist in many forms ranging from diamond and graphite (3D) to graphene (2D) [1], nanotubes (1D) [2] or fullerenes (0D) [3]. With the exception of diamond, it is possible to think of fullerenes, nanotubes and graphite as different structures built from the same hexagonal array of sp² carbon atoms which were reported to possess exceptional mechanical properties. As for thin film field, amorphous graphite like carbon (GLC) films with highly sp² bond structure were reported to demonstrate an excellent wear resistance and high load-bearing capacity meanwhile remaining a relatively high hardness. These properties make GLC an ideal coating for high-load wear applications and cutting tools especially for difficult machine materials.

Nowadays, amorphous GLC thin films are possible

to be fabricated by using numerous techniques including ion beam sputtering, magnetron sputtering, laser ablation and vacuum cathodic arc. All these techniques in common are aimed to generate an intense bombardment of energetic ions to control the formation of sp²/sp³ bond during the film growth. Therefore, it is of fundamental importance to understand the effect of substrate bias on the formed film structure especially sp³/sp² ratio.

One of the main problems for the further application of GLC films is the poor adhesion to different substrates. Previous studies showed that the adhesion and toughness in the films can be markedly increased by buffer layer and interlayer [4]. Magnetron sputtering, the traditional method to produce a buffer layer and interlayer, is a technique of neutral atom deposition, only a few of the sputtered atoms are ionized, so the adhesion is weak. High power impulse magnetron sputtering (HIPIMS) is an important physical vapor deposition (PVD) process in which the power density exceeds conventional power density by about three orders of magnitude. Electrostatic probe measurements show that plasma density of about

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10^{19} m^{-3} can be generated [5,6]. The fraction of ionized sputtered copper can approach to 70% [7]. Therefore, HIPIMS can provide a highly ionized flux of sputtered species, and thus a promising technique to prepare a buffer layer with good adhesion strength [7–10].

In this work, a hybrid system was used, which is composed of a direct current magnetron sputtering (dc-MS) source of carbon and a high power impulse magnetron sputtering (HIPIMS) source of Cr with reactive gas of C_2H_2 . The hydrogen-free GLC, Cr-doped GLC films (Cr-GLC) and the Cr-doped hydrogen-GLC films (Cr-GLC-H) were prepared for comparison. The influence of substrate bias on the Cr-GLC-H films was investigated to study the formed film structure and its tribological behaviors.

2 Experimental

High speed steel (HSS) and silicon (100) wafers were used as the substrate materials. All the substrates were cleaned ultrasonically in acetone and ethanol, and dried in air before being putted into the vacuum chamber. The films were prepared on the HSS and silicon substrates by a HIPIMS with a 120 mm×380 mm rectangular Cr target (99.99%) and DC magnetron sputtering with a 120 mm×380 mm rectangular C target (99.99%). Prior to deposition, the substrates were cleaned with Ar plasma sputtering at a bias voltage of 500 V for 20 min so as to remove the native oxide on the substrates. The base pressure was evacuated to a vacuum of 4×10^{-3} Pa.

In the preparation process, the HIPIMS with Cr target was used to prepare the Cr buffer layer with Ar as sputtering gas. Next, the HIPIMS with Cr target was used to prepare the CrC inter-layer with Ar as sputtering gas and C_2H_2 as reactive gas. Last, the DC magnetron sputtering source with a C target was used to prepare the GLC with Ar as sputtering gas. Cr doping was achieved by HIPIMS and C_2H_2 gas was introduced to form hydrogen containing films. Different negative bias voltages were applied to substrate for Cr-GLC-H films.

Raman spectroscopy with an incident Ar^+ beam at a wavelength of 514.5 nm was used to measure the atomic bonds of films. An X-ray photoelectron spectroscopy (XPS) with Al K_α irradiation at pass energy of 160 eV was used to characterize the chemical bonds and microstructure of the films. The thickness of the deposited films was measured by a step profiler. The tribological behaviors of the treated sample were investigated on a rotary ball-on-disk tribometer at room temperature under dry sliding conditions. Bearing steel with a diameter of 6 mm was used as the friction counter body. All the tests were performed at a sliding speed of 100 mm/s and the applied load was 3 N. An MTS

nano-indenter was performed to test the hardness and elastic modulus of the treated samples in this study.

3 Results and discussion

3.1 Chemical bonds structure of GLC films

The chemical bonds of the deposited films can be observed from the XPS spectra. Figure 1 shows the XPS C1s peaks of the pure GLC, Cr-GLC and Cr-GLC-H films. The final peak shape should be Lorentzian and Gaussian convolution of the Voigt peak shape obtained [11,12]. Fitted variables included sp^2 peak energy, sp^3 and sp^2 peak energy difference, and C—O and C=O peak energy of small fluctuations. These were the single

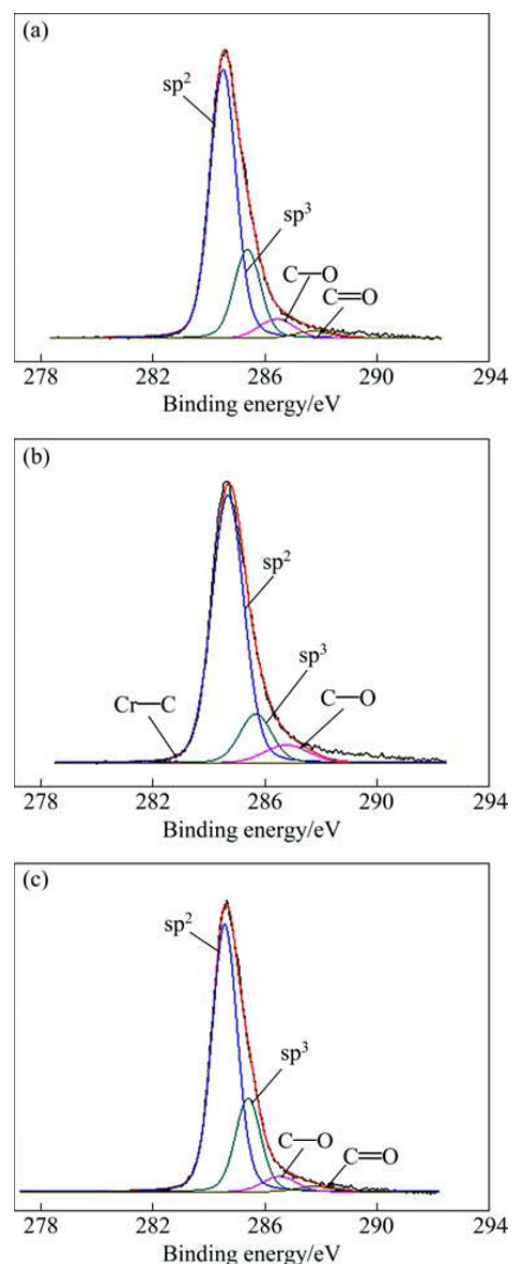


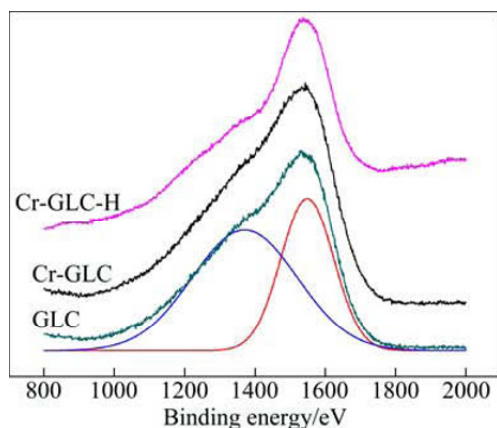
Fig. 1 XPS C1s spectra of GLC films: (a) Pure GLC film; (b) Cr-GLC film; (c) Cr-GLC-H film

Table 1 Bonding contents in GLC films

Type of film	Bonding content/%		
	sp ²	sp ³	C—O
GLC	68.891	22.904	8.205
Cr-GLC	78.954	14.343	6.703
Cr-GLC-H	69.129	24.371	6.500

C—O bond at 286.6 eV, the double C=O bond at 287.7 eV, the sp² bond at 284.6 eV, the sp³ bond at 285.4 eV and Cr—C bond at 283 eV (Cr₇C₃ at 283.1 eV, Cr₃C₂ at 282.94 eV, Cr₂C₃ at 282.8 eV etc.) [13]. The integration results are listed in Table 1, the sp² contents of the three GLC films are more than 65%. The content of sp² bond in GLC film increases when metal Cr is doped. And a small content of chromium carbide crystalline phase was detected in the amorphous carbon matrix of the film. As for Cr-GLC-H films, a slight decrease of sp² content is due to the fact that, C₂H₂ decomposes into carbon and hydrogen and forms C—H sp³ bonds.

Raman spectroscopy is a fast and nondestructive tool for characterization of amorphous carbons. All amorphous carbon show the common features in Raman spectra in the region of 800–2000 cm⁻¹, the so-called peaks G and D, which lie at around 1560 cm⁻¹ and 1360 cm⁻¹. The peak G is due to the bond stretching of all pairs of sp² atoms in both rings and chains. The peak D is due to the breathing modes of sp² atoms in rings [14,15]. As shown in Fig. 2, according to the intensity ratio of peak D to peak G (I_D/I_G), the sp²/sp³ ratio of the amorphous carbons films can be characterized [14]. As the sp²/sp³ ratio decreases in hydrogenated amorphous carbon, the I_D/I_G ratio will decrease. By integrating, the I_D/I_G is 1.578, 1.790 and 1.242 for GLC, Cr-GLC and Cr-GLC-H films, respectively. The ratio increases in the Cr-GLC film, implying that the sp²/sp³ ratio in the Cr-GLC films is higher than that in the GLC film. The increase of the sp²/sp³ ratio due to Cr doping might attribute to the catalyst effect of atoms on the formation of sp² sites. It is found that the Cr-GLC-H films show

**Fig. 2** Raman spectra with different types of GLC films

strong photoluminescence background (PL) in visible Raman spectroscopy due to the hydrogen saturation of the non-radiative recombination centers, which notes H element in the film[16]. The ratio decreased in the Cr-GLC-H films, implying that the sp²/sp³ ratio in the Cr-GLC-H films is lower than that in the Cr-GLC. The hydrogen is expected to correlate with sp³ fraction site, because the hydrogen preferable saturates the C=C sp² bonds and promotes the transformation from sp² sites to sp³ sites [17]. This is consistent with the XPS result.

3.2 Effect of substrate bias on microstructure of GLC films

Table 2 displays XPS results of the chemical bond composition with applied bias voltages. At -100 V bias voltage, the chromium content is near zero which might be caused by the “target poisoning” due to the interaction of the target with the C₂H₂. With a higher bias voltage, the phenomenon disappears. The chromium content is increased with an increasing bias voltage, during which more Cr ions are attracted towards the substrate. The oxygen in the films is due to O₂ within the vacuum chamber and films reacted with the O₂.

Table 2 Cr-GLC-H films composition with different bias voltages

Bias voltage/V	x(C)/%	x(Cr)/%	x(O)/%
-100	98.2	0	1.8
-150	87.35	4.9	7.75
-200	86.41	5.81	7.78
-250	86.16	5.89	7.95

Figure 3 presents the C1s and Cr2p XPS spectra of Cr-GLC-H films with different applied bias voltages. As the bias voltage is -100 V, the Cr2p has no peak which is due to target poisoning. When the voltage is higher than -100 V, the Cr2p shows a major peak at a binding energy around 574 eV and a shoulder around 583.7 eV. Actually, it is difficult to identify the chromium carbide in Cr2p. The C1s peak is combined to determine the chromium carbide. There is no peak around 283 eV, which means the metal chromium atoms distributing in the Cr-GLC-H films. The relative intensity of C1s peak has a maximum value at -100 V, which again verifies the occurrence of target poisoning and causes a low content of carbon.

The integration sp² bond at 284.6 eV and sp³ bond at 285.4 eV are shown in Fig. 4. The sp² content is firstly decreased and then increases, and the sp³ content is just the reverse. This variation trend consists of a chemical adsorption process of the species on the growing surface and a physical process of implantation at the subsurface, which mainly depends on the ion energy. At a low bias voltage, the ion energy is too weak to penetrate into the growing surface and most of the ions are trapped on the

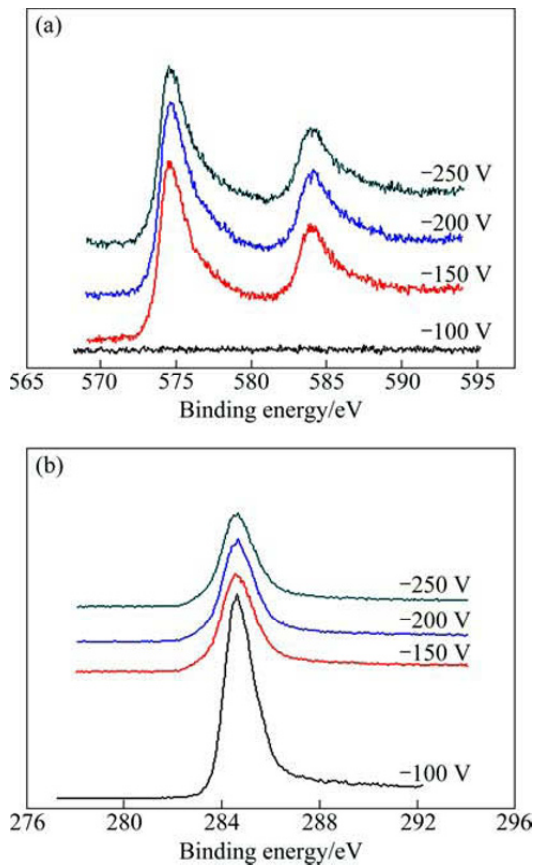


Fig. 3 Cr2p and C1s XPS spectra of Cr-GLC-H films with different bias voltages

growing surface, resulting in the formation of the sp^2 bond. Increasing the negative bias voltage to -150 V, the ion species will have sufficient energy ($80\text{--}100$ eV per atom) to penetrate into the subsurface. Under this condition, the sp^2 bond turns to the sp^3 bond. However, at higher bias voltage more than -150 V, the dissipation of

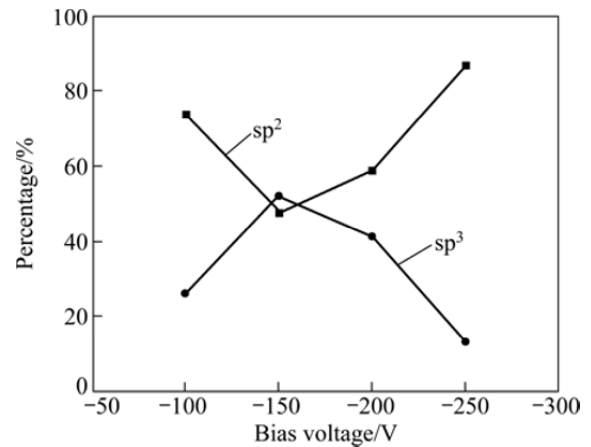


Fig. 4 C bonding percentage with different bias voltages

the excess heat generated by impinging the energetic ions can relax the high compressive stress that leads to loose carbon networks, which leads to the sp^3 to sp^2 bonds transformation.

AFM images shown in Fig. 5 illustrate the effect of the bias voltage on the Cr-GLC-H surface roughness and feature. With the bias voltage at the range from -100 V to -250 V, the surface roughness in turn is 2.52 , 3.78 , 3.50 , 3.08 nm, respectively. The films deposited at all applied bias voltages show very smooth and flat surfaces, which are benefited from this hybrid HIPIMS technique. The surface of the Cr-GLC-H films is the smoothest at bias voltage of -100 V. Under this condition, the HIPIMS Cr target is target poisoning, and there is no collisional damage of Cr ions with high energy to the carbon network, resulting in a low roughness. The surface roughness further decreases with the voltage increased from -150 V to -250 V. This decreasing tendency of surface roughness was reported previously.

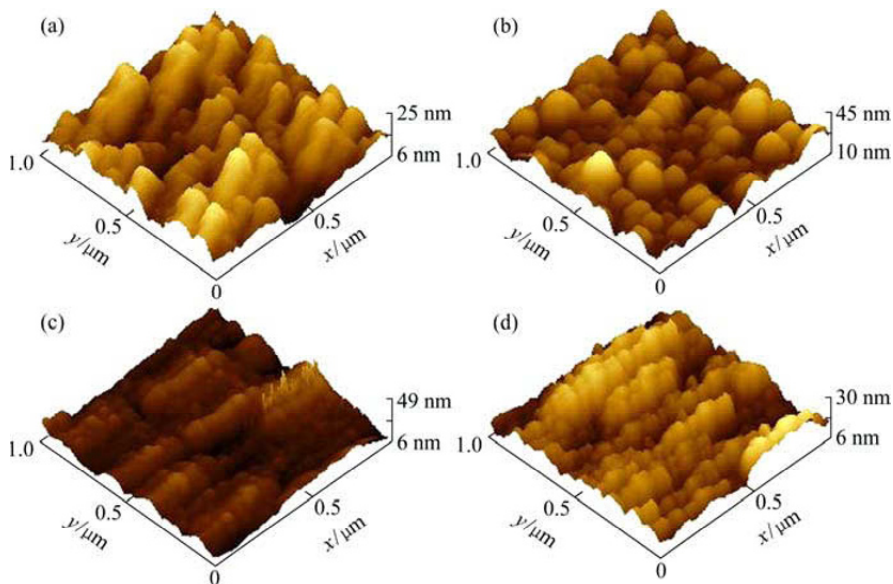


Fig. 5 AFM images of Cr-GLC-H film at different bias voltages: (a) -100 V; (b) -150 V; (c) -200 V; (d) -250 V

It might be related with the high energy of impinging ions to film growth that help improve the roughness by the surface diffusion [18].

3.3 Effect of substrate bias on tribological behavior of GLC films

The low friction coefficient and long wear life of GLC films play an important role for its industrial applications. Figure 6 shows the average friction coefficient of Cr-GLC-H films with different bias voltages. With the bias voltage increasing, it can be found an increase (up to maximum at -150 V) and subsequent decrease of the friction coefficient. The change trends of sp^3 bond, surface roughness and friction coefficient with the increased bias voltages are the same in variation. The lowest surface roughness and lowest friction coefficient correspond to the highest sp^3 with the Cr-GLC-H films at the bias voltage of -100 V. It should be noted here that the calculated wear rate of Cr-GLC-H films has the minimum value of $9.85 \times 10^{-11} \text{ mm}^3/(\text{N}\cdot\text{m})$ at -100 V of bias voltage.

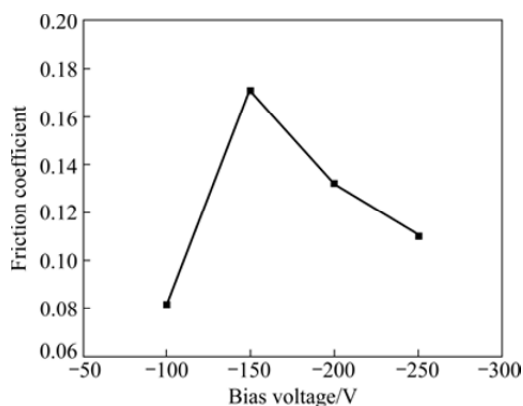


Fig. 6 Friction coefficients of Cr-GLC-H films deposited with different bias voltages

4 Conclusions

The GLC films were successfully deposited on HSS and silicon wafers by a hybrid HIPIMS with DC-MS technique. The results showed that Cr doping increased the content of the sp^2 bonds, and hydrogen content would cause an increase of sp^3 -type bonding. With the bias voltage increased, it can be found a first increase (up to maximum at -150 V) and a subsequent decrease of sp^3 bond, surface roughness as well as friction coefficient of Cr-GLC-H films. At the bias of -100 V, Cr-GLC-H films demonstrated a low friction coefficient and wear rate.

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