Microstructure and surface properties of chromium-doped diamond-like carbon thin films fabricated by high power pulsed magnetron sputtering

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A B S T R A C T

High power pulsed magnetron sputtering (HPPMS) has attracted much interest due to the large plasma density and high ionization rate of sputtered materials. It is expected to produce a highly ionized C flux from a graphite target but unfortunately, the ionization rate of carbon is still very small and the discharge on a solid carbon target is unstable as well. In this work, a stable discharged chromium target is used in the preparation of chromium-doped diamond-like carbon (Cr-DLC) films in HPPMS in reactive C2H2 gas, but the unstable graphite. The chromium concentration in the Cr-DLC films is limited by surface poisoning due to reactive gas. Less than 2% of Cr is incorporated into the DLC films at C2H2 flow rate of 5 sccm or higher. However, as a result of the high ionization rate of the reactive gas in HPPMS, intense ion bombardment of the substrate is realized. The films show a smooth surface and a dense structure with a large sp3 concentration. As the C2H2 flow increase, the sp3 fraction increase and the sp3 to sp2 ratio increase to 0.75 at a C2H2 flow rate of 10 sccm. Compared to the substrate, the Cr-DLC films have lower friction and exhibit excellent corrosion resistance.

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1. Introduction

DLC films have widespread applications as protective coatings in cutting tools, molds, optical windows, magnetic storage disks, and micro-electromechanical devices (MEMs) due to their high mechanical hardness, chemical inertness, and wide band gap.[1–3] Most of the key properties of DLC stem from the sp3 component which can be enhanced by ion bombardment.[4,4] Thus, a highly ionized and energetic carbon flux should bode well for the deposition of DLC films with the desirable properties.

High power pulsed magnetron sputtering is considered a highly ionized physical vapor deposition technique[5,6] which can produce highly ionized fluxes similar to those produced by arc evaporation sources but without excessive heating and droplet formation.[7,8] Therefore, HPPMS has been utilized to get highly ionized carbon fluxes from pure graphite target. For example, Münz, et al. [9] fabricated several kinds of DLC films using a device equipped with the HPPMS cathode. Schmidt, et al. [10] and Lattemann, et al. [11] also tried to prepare DLC films by HPPMS, but unfortunately, the ionization rate of carbon from a graphite cathode was very low and the discharge on the C cathode was also unstable.[12] In fact, carbon containing gases such as CH4 and C2H2 can be ionized much more easily than a graphite cathode in HPPMS.[13] Besides, HPPMS can produce an ion flux with significant larger amounts of ionized film-forming species in a reactive gas atmosphere.[14] Therefore, carbon containing gases may be a good choice in the preparation of DLC by HPPMS.

To achieve a steady discharge containing excited carbon species, a metal magnetron target, which is easily ignited, ought to be employed and this will result in metal doped DLC films. There have been many reports stating that the adhesion and other properties of DLC can be improved by doping with metallic or nonmetallic elements, such as Ti, [15,16] W, [17,18] Cu, [19] Cr, [20,21] C, [22] N, [23] Ar, [24] and so on, and among these elements, chromium shows the most intense and steady discharge in HPPMS configuration.[12] In this paper, a Cr cathode is employed to stabilize the discharge in a mixed atmosphere of Ar and C2H2 to deposit DLC films by HPPMS. By controlling the C2H2 flow rate, only a small content of Cr is introduced to the DLC films. The surface micrography, microstructure and other surface properties of the Cr-doped DLC (Cr-DLC) films are investigated.

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2. Experimental details

The experiments were performed in a vacuum chamber with a diameter of 40 cm and height of 40 cm evacuated by a molecular pump to a base pressure of $3 \times 10^{-3}$ Pa. The carrier gas (Ar, 99.9997% pure) and reactive gas ($C_2H_2$, 99.998% pure) were introduced through a mass flow meter. Fig. 1 shows the schematic diagram of the HPPMS equipment. A Cr target (50 mm in diameter, 6 mm in thickness, and 99.9% pure) was mounted on an unbalanced magnetron cathode. The magnetron cathode was driven by a hybrid pulsed power supply developed in our laboratory. [25] Silicon (1 0 0) and SUS304 stainless steel samples (30 × 30 mm²) were used as substrates. Prior to loading into the chamber, the substrates were ultrasonically cleaned in ethanol and acetone for 20 min. The substrates were placed at a distance of 12 cm from the target and no external heating was applied during the process. Plasma etching was performed using a high-voltage self-excited glow discharge in argon. Afterwards, a Cr layer was deposited on the substrates by HPPMS in argon to increase the adhesion between the film and substrate. $C_2H_2$ was gradually introduced into the chamber to produce the Cr/CrC$_x$/Cr-DLC multilayered structure for good adhesion until the required ratio of Ar to $C_2H_2$ was reached. The thicknesses of inter Cr layer, gradient CrC$_x$ layer, and outer Cr-DLC layer were 194 nm, 130 nm and 1.74 μm, respectively. The important processing parameters are listed in Table 1.

A digital oscilloscope was used to monitor the target voltage and current. The microstructure of the films was examined by scanning electron microscopy (SEM, Hitachi S4800). Unbalanced information was obtained on a micro Raman scattering instrument (LabRAM HR800, HORIBA Jobin Yvon) between 300 cm$^{-1}$ and 3000 cm$^{-1}$ and an X-ray photoelectron spectroscopy (XPS, PHI-5802) with monochromatic Al Kα radiation. The phase composition of the films was determined by X-ray diffraction (XRD, D8 ANVANCE) in the Bragg-Brentano geometry. The wear resistance of the samples was evaluated by a home-made ball-on-disk tester under ambient conditions (relative humidity of 25 ± 1% RH and temperature of 20 ± 1°C) by sliding against a Φ 6 mm Cr13 ball at a load of 100 g, speed of 50 r/min, and a wear radius of 2 mm. The corrosion resistance of the films was investigated by potentiodynamic polarization tests in a 3% NaCl solution using a CHI604C system.

3. Results and discussion

Fig. 2 shows the $I$–$V$ curves of the Cr target in the HPPMS mode. After the onset of the pulse, the current of the target increases rapidly to about 50 A at about 100 μs after the initial current rise and then decreases slowly due to the gas rarefaction effect. [26] After the pulse, the discharge current drops to zero within 20 μs. The discharge is stable and reproducible in the experiments.

The Cr-DLC films have a bright black color. Fig. 3(a) and (b) depict the surface and cross-sectional micrographs of the Cr-DLC films produced at Ar to $C_2H_2$ ratio of 10 to 10. The film surface is dense, uniform, and free of holes or micro-particles. The cross-sectional Si/Cr/CrC$_x$/Cr-DLC structure displayed in Fig. 2(b) suggests effective release of residual stress and good adhesion between the film and substrate. [15,19,20,27]

As described in Section I, the Cr content in the as-deposited DLC films is controlled by introducing $C_2H_2$ which poisoned the chromium target. Fig. 4 shows the composition of the top surface of Cr-DLC films prepared by HPPMS with different Ar/$C_2H_2$ ratios determined by XPS. The Cr concentrations decrease with increasing $C_2H_2$ flow due to the surface reaction on the Cr target in the reactive atmosphere. The C and Cr concentrations in the films change slightly when the $C_2H_2$ flow is changed to 5 sccm or larger but decreased to 1.72% at a $C_2H_2$ flow rate of 10 sccm. Besides, there is about 18% oxygen in the films as a result of contamination from the residual vacuum.

Raman scattering is a popular and effective tool to characterize the carbon bonding in DLC films. Fig. 5 depicts the Raman spectra of the Cr-DLC films as a function of Ar to $C_2H_2$ gas flow ratios between 1000 and 1800 cm$^{-1}$. All the spectra exhibit asymmetric

<table>
<thead>
<tr>
<th>Step</th>
<th>Process</th>
<th>Parameters</th>
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<tbody>
<tr>
<td>1</td>
<td>Plasma etching</td>
<td>Ultimate vacuum = 1.0 \times 10^{-3} Pa, High voltage pulse = –10 kV, Frequency = 50 Hz, width = 200 μs, Ar flow rate = 10 sccm, Working pressure = 1.0 Pa, 20 min</td>
</tr>
<tr>
<td>2</td>
<td>Cr interlayer</td>
<td>HPPMS pulse = 900 V, Frequency = 50 Hz, width = 200 μs, DC = 0.2 A, Ar flow rate = 10 sccm, Working pressure = 0.5 Pa, T = 5 min, Bias = –100 V</td>
</tr>
<tr>
<td>3</td>
<td>Cr-DLC film</td>
<td>HPPMS pulse = 900 V, Frequency = 50 Hz, width = 200 μs, DC = 0.2 A, Ar flow rate = 10 sccm, $C_2H_2$ flow rate = 2.5, 5, 7.5, 10 sccm, Working pressure = 0.5 Pa, T = 50 min, Bias = –100 V</td>
</tr>
</tbody>
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dispersion indicative of DLC. The G peak at around 1580–1600 cm\(^{-1}\) and D peak at around 1350 cm\(^{-1}\) are usually assigned to zone center phonons of the \(E_{2g}\) symmetry and K-point phonons of \(A_{1g}\) symmetry, respectively. [28,29] With increasing \(C_2H_2\) flow, the intensities of the Raman peaks are enhanced obviously.

To investigate the film properties, the Raman spectra are deconvoluted into two Gaussian peaks denoted as G and D. [30] Fig. 6 shows the relative intensity of the D-band to the G-band together with the locations of D peak and G peak in the Raman spectra of the Cr-DLC films. For the film deposited at a \(C_2H_2\) flow rate of 2.5 sccm, the G peak is centered at 1558.4 cm\(^{-1}\) and shifts to smaller wave numbers in a small range when the \(C_2H_2\) flow rate is increased from 2.5 to 10 sccm. The G peak shifts considerably from 1580 cm\(^{-1}\) in pure graphite to 1550 cm\(^{-1}\) in DLC, and the locations of the G peak depends on the \(sp^3\) content in the DLC films. [31] Therefore, the smaller wave numbers of the G peak and shift suggest that the \(sp^3\) content in the DLC films is large and it increases with larger \(C_2H_2\) flow rates. The ratio of the area under the D-peak to that of the G-peak is small and it decreases with the increasing \(C_2H_2\) flow rates, thus indicating a larger \(sp^3\) component. [32]

Fig. 7 displays the high-resolution C1s XPS spectra of Cr-DLC films produced by HPPMS using different \(Ar/C_2H_2\) ratios. As the \(C_2H_2\) flow rates go up, the C1s peak shifts from 284.47 eV toward 284.56 eV implying increased \(sp^3\) content. All the spectra show binding energies of 282.8 eV for the Cr\(_3\)C\(_2\) bond, 284.15 eV for \(sp^2\) bond, and 285.3 eV for \(sp^3\). [33,34] The relative contents of the three types of bonds and \(sp^3/sp^2\) ratio determined by integrating the related peak intensity in the C1s spectra are shown in Fig. 8.
A small amount of Cr$_3$C$_2$ exists in the DLC film prepared at a C$_2$H$_2$ flow rate of 2.5 sccm but almost disappears when the C$_2$H$_2$ flow rate is larger than 5 sccm. With increasing C$_2$H$_2$ flow, the fraction of sp$^3$ increases and the sp$^3$/sp$^2$ ratio is up to 0.75 at a C$_2$H$_2$ flow rate of 10 sccm.

The large sp$^3$ fraction in the Cr-DLC films stem from the highly ionized plasma in HPPMS and energetic ion bombardment. With regard to the latter, various mechanisms such as preferential sputtering, [35] shock wave effect, [36] subplantation, [37] and so on, [38,39] synergistic enhances the formation of the sp$^3$ bonds. Fig. 9 shows the XRD spectra acquired from the Cr-DLC films prepared by HPPMS using different Ar/C$_2$H$_2$ ratios. In addition to the peak arising from the Si substrate, several weak peaks such as Cr$_3$C$_2$ (2 0 4), Cr$_3$C$_2$ (2 1 5) and Cr$_2$O$_3$ (3 1 2) can be observed [40,41] and they arise from carbonization and oxidation of chromium in the films. Chromium oxide exists in the chemical form of Cr$_2$O$_3$ instead of Cr$_2$O$_5$ [42] possibly due to the intense discharge, high ion energy, and local high temperature during HPPMS. [41,43] As the C$_2$H$_2$ flow rate is increased, the intensity of the carbide peaks decrease and almost the peaks also vanish at C$_2$H$_2$ flow rates higher than 5 sccm. This is consistent with the XPS results shown in Fig. 7. No pure carbon peak can be observed, indicating that nearly the carbon is in the amorphous state in the films. [44] Furthermore, the oxide detected by XRD may be due to the small oxidation potential of Cr and surface contamination.

Fig. 10 shows the hardness of the Cr-DLC films produced by HPPMS using different Ar/C$_2$H$_2$ ratios. The hardness of the Cr-DLC films increased to 26 GPa as the Ar/C$_2$H$_2$ flow ratios change from 10/2.5 to 10/10. The hardness is about 5 times that of the stainless steel substrate. The wear resistance of the films is evaluated on a ball-on-disk tester. The friction coefficients and the wear traces acquired from the film produced using an Ar/C$_2$H$_2$ ratio of 10/10 and substrate (for comparison) are shown in Fig. 11. The friction coefficient of the film is quite small and about 0.1 throughout the 9-hour test. Compared to SU304 stainless steel, the wear trace of the film is narrow and shallow. The average friction coefficients of the samples are listed in Table 2 which shows that as the C$_2$H$_2$ flow rate is increased, the average friction coefficient diminishes.

The corrosion resistance is determined by monitoring the corrosion potentials and currents and the results are displayed in Table 2. HPPMS is expected to yield dense and smooth films with improved corrosion resistance. [45] Compared to the SU304 stainless steel substrate, the coated samples exhibit higher corrosion potentials and smaller corrosion currents and excellent corrosion resistance is revealed. In fact, the corrosion resistance improves with increasing the C$_2$H$_2$ flow.
4. Conclusion

Cr-doped DLC films are prepared by HPPMS using a Cr target in mixed atmosphere of Ar and C2H2. The Cr-DLC films have a smooth surface and dense structure with large sp3 to sp2 ratio due to high ionization rate of the reaction gas in HPPMS and intense ion bombardment of the substrate. Gradual interfacial transition is observed from the cross-sectional micrographs and Cr2C3 is formed by adjusting the C2H2 flow rate which in turn dictates the poisoning effects on the Cr target. The DLC films are doped with 1.75% Cr atoms in the top surface and as the C2H2 flow rate increase, sp3 fraction goes up. Compared to the substrate, the coated samples exhibited a smaller friction coefficients and better corrosion resistance.

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