Deposition and properties of Al-containing diamond-like carbon films by a hybrid ion beam sources

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ABSTRACT

Metal incorporation is one of the most effective methods for relaxing internal stress in diamond-like carbon (DLC) films. It was reported that the chemical state of the incorporated metal atoms has a significant influence on the film internal stress. The doped atoms embedding in the DLC matrix without bonding with C atoms can reduce the structure disorder of the DLC films through bond angle distortion and thus relax the internal stress of the films. In present paper, Al atoms, which are inert to carbon, were incorporated into the DLC films deposited by a hybrid ion beams system comprising an anode-layer ion source and a magnetron sputtering unit. The film composition, microstructure and atomic bond structure were characterized using X-ray photoelectron spectroscopy, transmission electron microscopy and Raman spectroscopy. The internal stress, mechanical properties and tribogoical behavior were studied as a function of Al concentration using a stress-tester, nanoindentation and ball-on-disc tribo-tester, respectively. The results indicated that the incorporated Al atoms were dissolved in the DLC matrix without bonding with C atoms and the films exhibited the feature of amorphous carbon. The structure disorder of the films tended to decrease with Al atoms incorporation. This resulted in the distinct reduction of the internal stress in the films. All Al-DLC films exhibited a lower friction coefficient compared with pure DLC film. The formation of the transfer layer and the graphitization induced by friction were expected to contribute to the excellent friction performance.

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1. Introduction

Diamond-like carbon (DLC) films have potential widespread applications in many industrial fields of cutting tools and dies, magnetic data storage, micro-electromechanical devices (MEMS) due to their outstanding properties, such as high hardness, low friction coefficient, good corrosion-resistance, and smooth surface [1–3]. However, the existence of the high internal stress in the films leads to poor adhesion to the substrate, and limits the extended utilization of DLC films [4–7]. The incorporation of metal atoms, which was expected to effectively reduce internal stress, has been attracted great interest for many years in the scientific community. Numerous metallic elements, including W [8], Ti [9], Cr [10] etc., which can combine with carbon to form carbide, and Al [11], Cu [12] etc., which are relatively inert to carbon, have been attempted as doped metal elements to reduce the internal stress and modify the properties of DLC films. Wang and co-workers [8] have studied the influence of W doping on the film internal stress and mechan-

ical hardness by a hybrid ion beams deposition system and found that the hardness was not sensitive to the W concentration, while the internal stress was strongly dependent on the chemical state of the incorporated metal atoms, and it showed a significant reduction when the W atoms were dissolved in the DLC matrix without bonding with C atoms, but the stress increased significantly as the W–C bonding was formed at high W concentration doping. It is supposed that the doped metals without interacting with carbon will do not affect the film microstructure by destroying the carbon network, and therefore the superior mechanical properties of the films that depend on the carbon network will be retained, while the internal stress can be reduced sharply through metal atoms doping.

Al is relatively inert to carbon and difficult to form carbide when incorporated into to DLC films. Accordingly, Al may be one of the best candidates for metal atom addition in stress relaxation. In present work, Al atoms were incorporated into DLC films using a hybrid ion beams system. The influences of Al incorporation on the microstructure and carbon atomic bond structure of the films were investigated as a function of Al concentration and the relationships among the microstructure, internal stress, hardness and tribological behavior have been studied carefully.

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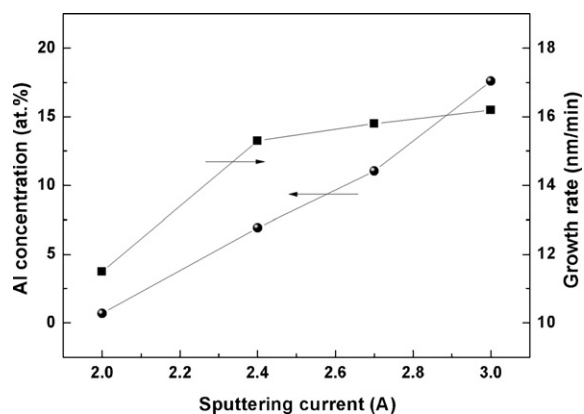 E-mail address: aywang@nimte.ac.cn (A. Wang).

Fig. 1. Al concentration and growth rate of the films as a function of sputtering current.

Fig. 2. Typical XPS C 1s peaks of the films with different Al concentration.

2. Experimental details

Al-DLC films were deposited by a linear anode-layer ion source combining with magnetron sputtering unit [13]. The C_2H_2 gas of 10 sccm was introduced into the ion source to obtain the hydrocarbon ions. Typical values of the discharge voltage and current of the ion source were 1650 V and 0.2 A, respectively. The Ar gas of 70 sccm was supplied to the magnetron sputtering equipped with an Al target (99.99%). A DC power (under current control model) was supplied to the magnetron sputtering. The Al concentration in the Al-DLC films was varied by changing the sputtering current from 2 A to 3 A. $525 \pm 15\,\mu m$ thick Si (1 0 0) wafers of size 20 mm × 20 mm were used as the substrates. In addition, $285 \pm 5\,\mu m$ thick silicon wafers of size 3 mm × 35 mm were also used as the substrates to accurately estimate the internal stress from the observed curvature of the film/substrate composite with Stoney equation [14] and the curvature of the film/substrate was determined by a laser tester. All the silicon substrates were cleaned ultrasonically in acetone for 10 min, and then dried in air. Before deposition, the chamber was evacuated down to 2.7×10^{-3} Pa, and then the Si wafers were sputter-cleaned for 10 min using Ar^+ ions. During the film deposition, the working pressure was about 0.5 Pa, and a pulse negative bias voltage of -50 V (350 kHz, 1.1 μs) was applied on the substrates. The deposition time was 1 h. For comparison, pure DLC film was also prepared using the ion source and a negative substrate bias of -50 V without operating the magnetron sputtering.

The thickness of the deposited films was measured using a surface profilometer (Alpha-step IQ, US) employing a step formed by a shadow mask and the film thicknesses are ranging from 700 to 1000 nm. The composition and chemical bonds of the deposited films was analyzed by X-ray photoelectron spectroscopy (XPS, Axis ultraDLD) with Al (mono) Kα irradiation at pass energy of 160 eV. Before commencing the measurement, Ar^+ ion beam with a energy of 3 KeV was used to etch the sample surface for 5 min to remove contaminants. The Al/C atomic ratio of the films was determined based on the atomic sensitivity factors and area ratio of the C 1s to Al 2p peaks in XPS spectra of the films, and the hydrogen atom concentration was not considered due to its signal intensity below the XPS detection threshold. High-resolution transmission electron microscopy (TEM) of the films was performed on Tecnai F20 electron microscope, which was operated at 200 KeV with a point-to-point resolution of 0.24 nm. The specimens for TEM analysis, with thicknesses of about 60 nm, were deposited directly on freshly cleaved single-crystal NaCl wafers, and then were peeled off through dissolving these NaCl wafers in deionized water. Raman spectroscopy with an incident Ar^+ laser at a wavelength of 514.5 nm was used to assess the carbon atomic bonds in the films.

Mechanical properties of the films were tested by the nano-indentation technique (MTS-G200) in a continuous stiffness measurement (CSM) mode with a maximum indentation depth of 500 nm. The characteristic hardness was chosen in the depth where the measured value was not affected by the soft Si substrate. A rotary ball-on-disk tribometer was employed to characterize the films tribological behavior at room temperature with a relative humidity of about 50%. A steel ball (SUJ-2, HRC60) with a diameter at 7 mm was used as the friction counter ball. All the tests were performed at 0.2 m/s sliding velocity for a distance of 300 m and the applied load was 3 N. After the friction test, the wear tracks were analyzed using SEM and XPS.

3. Results and discussion

3.1. Composition and microstructure

Fig. 1 shows the Al concentration and the average growth rate of the films as a function of sputtering current. It can be seen that both the Al concentration and growth rate of the deposited films increase
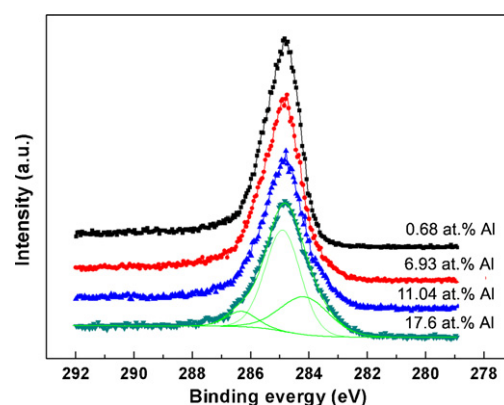
linearly with the sputtering current. As the current increases from 2 A to 3 A, the Al concentration of the films increases from 0.68 to 17.6 at.% and the growth rate of the films increases from 11.5 to 16.2 nm/min. It seems that the Al incorporation would improve the growth rate of the films deposited by the hybrid ion beams.

Fig. 2 shows the XPS C 1s spectrums of the Al-DLC films with different Al concentration. There is a major peak at a binding energy around 284.5 eV, which represents the typical binding energy of the DLC films [15]. The C 1s spectra can be deconvoluted into three components around 284 eV, 285 eV and 286 eV corresponding to sp^2–C, sp^3–C and C–O, respectively [16]. Generally, the C 1s spectra of the aluminum carbides have binding energies lower than 283.0 eV (e.g. 281.5 eV for Al–C and 282.5 eV for A–O–C) [16,17]. However, these reported peaks were not observed in present experiments. This indicates that the Al-DLC films also reveal an amorphous carbon structure as the pure DLC. It should be noted that the full width at half maximum (FWHM) of the C 1s peaks and the sp^2/sp^3 related peak area ratio in the C 1s spectra of the films increase with Al concentration, which implies that the incorporation of Al can result in the increase of the graphitic component (sp^2–C fraction) in the films.

Fig. 3 shows the TEM micrograph and corresponding selected area electron diffraction (SAED) pattern of the films with 0.68 and 17.6 at.% Al. Fig. 3(a) and the insert of the magnified view exhibit dense and smooth granular contrasts, and the corresponding SAED shows a broad and diffuse diffraction halo pointing out a typical amorphous feature. For the film with 17.6 at.% Al, it is characteristic to note that numerous stripes are presented, as shown in Fig. 3(b). The inserted magnified view indicates that the stripe perhaps may be the Al-enrich clusters, which were separated from the DLC matrix due to excess Al concentration at high sputtering current. However, the corresponding SAED also reveals a diffuse halo without any observable diffraction rings.

Raman spectroscopy is a useful tool to obtain the detailed carbon bonding structure of the DLC films. Fig. 4(a) shows the representative Raman spectrums of the Al-DLC films with different Al concentration. There is a broad asymmetric Raman scattering band in the range from 1000 to 1700 cm^{-1}, representing the typical characteristic of DLC films [1]. The DLC Raman spectra can be fitted by two Gaussian peaks, D peak around 1350 cm^{-1} and G peak around 1550 cm^{-1}. The D peak is due to the breathing modes of sp^2 atoms only in aromatic rings, but the G peak is due to the bond stretching of all pairs of sp^2 atoms in both aromatic rings and chains, so the intensity ratio of D peak to G peak (I_D/I_G) will increase as the graphitic component increased [1].

Fig. 4(b) presents the ratio of I_D/I_G as a function of Al concentration. It can be seen that as the Al concentration increases, the I_D/I_G increases monotonously. This indicates that the films tend to be graphitizing with the Al concentration increasing, consistent
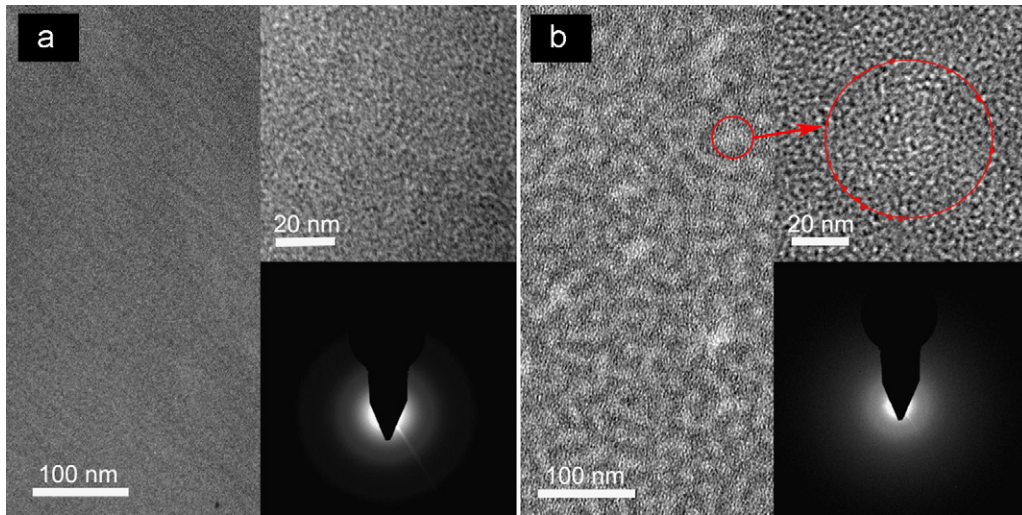
Fig. 3. TEM micrograph and corresponding SAED pattern of the films with (a) 0.68 at.% and (b) 17.6 at.% Al.
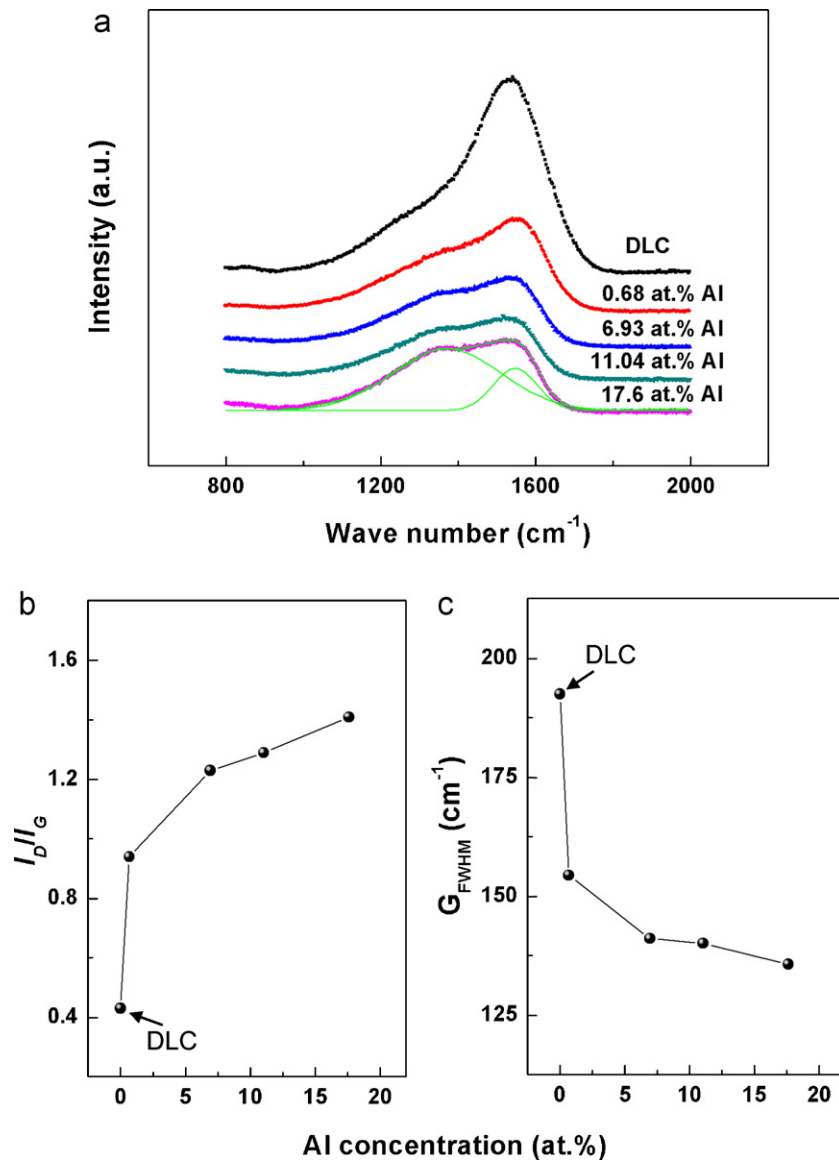

Fig. 4. (a) Representative Raman spectra, (b) corresponding I_D/I_G ratio and (c) G_{FWHM} of the films as a function of Al concentration.
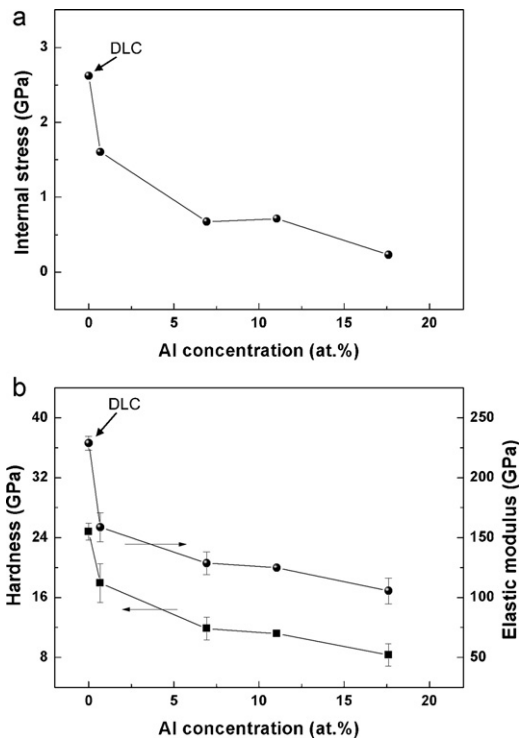
Fig. 5. (a) Internal stress and (b) hardness and elastic modulus of the films as a function of Al concentration.

with the XPS results. Furthermore, the FWHM of G peak (G_{FWHM}) is expected to be sensitive to structural disorder that arose from bond angle and bond length distortions [18]. The G_{FWHM}, as Fig. 4(c) shows, decreases monotonously with increasing Al concentration. This implies that the structure disorder of the films decreases as the Al concentration increases. It was reported that the metal atoms embedding in the DLC matrix without forming carbide bonds could play a pivotal site, whereby the distortion of the bond angles can
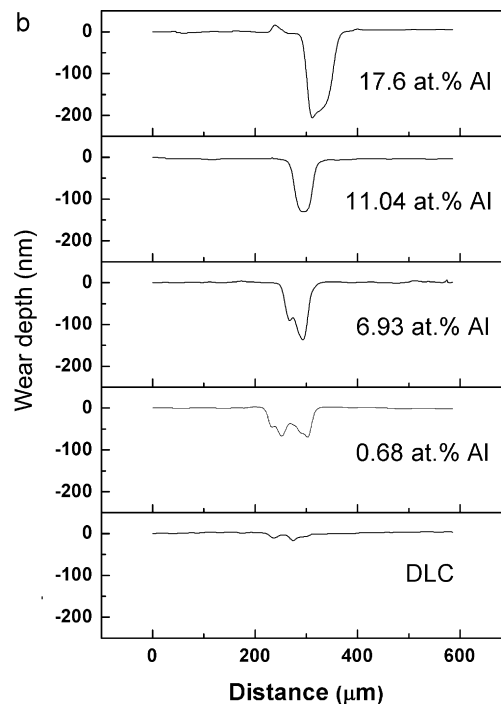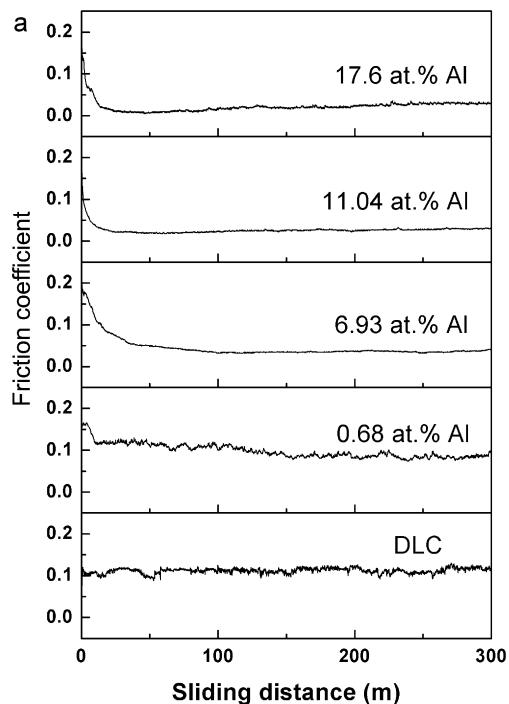

Fig. 7. Average friction coefficient and wear rate of the films as a function of Al concentration.

occur [8]. As a result, the films tend to be graphitizing and ordering under the Al incorporation.

3.2. Stress and mechanical properties

Fig. 5(a) presents the internal stress of the films as a function of Al concentration. The internal stress of the Al–DLC films shows a significant reduction compared with that of the pure DLC film, and it decreases subsequently with Al concentration increasing. Normally, the internal stress is thought to arise from the formation of sp^3 bonds that correlate with the structure disorder of the atomic bond angles and bond length during the film deposition [1]. One hand, the reduction of the internal stress should be attributed to the decrease of the structure disorder due to Al incorporation. According to the Raman results, the incorporation of Al atoms can decrease the film structure disorder through the distortion of the atomic bond angles, and thus cause the internal stress of the film to decrease. On the other hand, the Me–C bonding, which would increase the internal stress, was not formed in the films [8]. Accordingly, the internal stress of the films decreases with increasing Al concentration.

Fig. 6. (a) Friction coefficient of the films as a function of sliding distance and (b) corresponding surface profiles of the wear tracks after friction test.
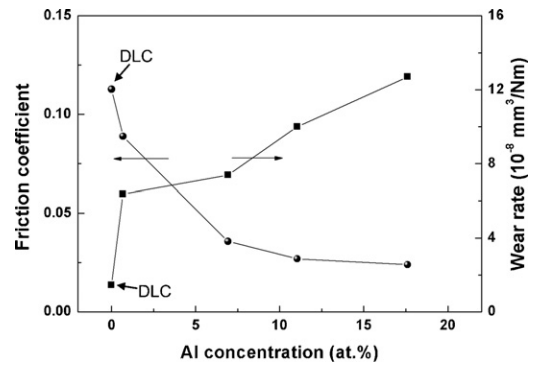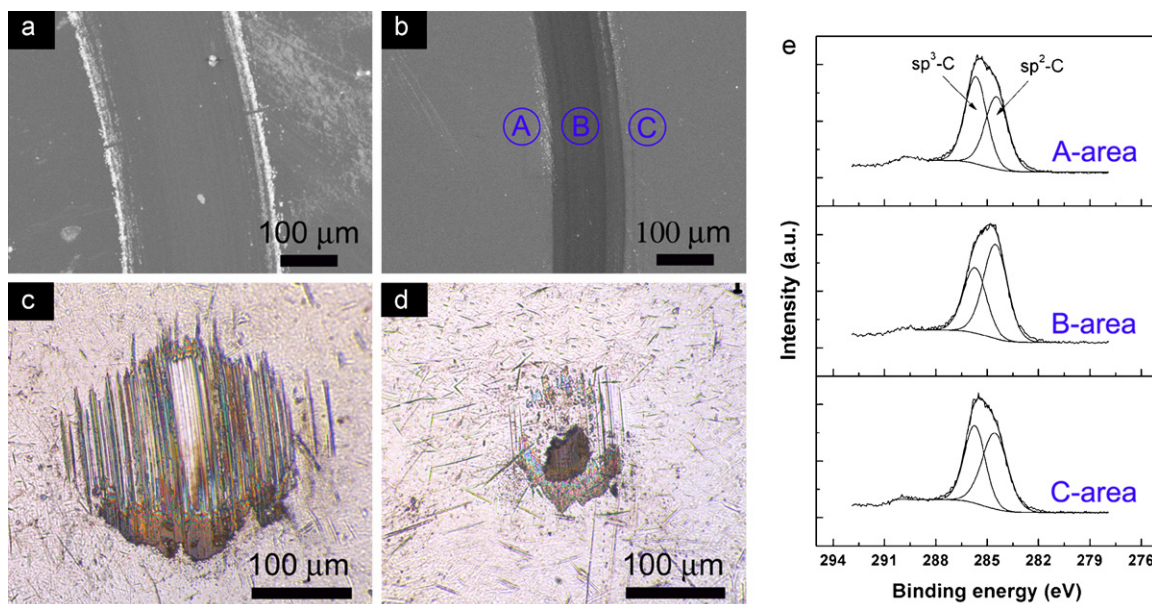
Fig. 8. SEM morphology of the wear tracks on (a) DLC and (b) Al-DLC with 11.04 at.% Al; optical micrograph of the corresponding contact ball of (c) DLC and (d) Al-DLC with 11.04 at.% Al; (e) XPS C 1s analysis on the area around the wear track of the Al-DLC as shown in (b).

The dependences of the film hardness and elastic modulus on Al concentration are shown in Fig. 5(b). It is seen that the variation in the film hardness with Al concentration is similar to that for the internal stress. The Al-DLC films also exhibit a significant reduction in the hardness compared with the DLC film. The mechanical properties of DLC films mainly depend on the sp^3 bond fraction in the films [1]. Considering the results of the XPS, the sp^2/sp^3 ratio increases with increasing Al concentration. This may be the main reason accounting for the decline of the hardness. Although both the internal stress and hardness decreases with increasing Al concentration, the internal stress drops faster than the hardness in present Al concentration range. These results indicate that Al incorporation could be effective to relax internal stress without changing the DLC film excellent mechanical properties significantly.

3.3. Tribological behavior

Fig. 6 presents the friction coefficient of the films against sliding distance and the wear tracks on the films after friction test. The average friction coefficients (calculated after 100 m of sliding distance) and wear rate of the films are shown in Fig. 7. Generally, the Al-DLC films show a lower friction coefficient compared with the DLC film (about 0.113). As the Al concentration increases from 0.68 to 17.6 at.%, the friction coefficient drops from 0.089 to 0.024. However, the wear tracks of the Al-DLC films on the films are deeper and broader than that of pure DLC film, and as the Al concentration increases, the wear rate of the films increases monotonously.

The wear behavior of the films may correlate with the film hardness. The incorporation of Al atoms reduces the film hardness and thus causes the film to be worn easily. Fig. 8 shows the typical SEM morphology of the wear tracks on the films and the optical micrograph of the wear scars on the contact balls. For the DLC film, it presents a low track, but its corresponding contact ball shows a big wear scars, which implies that the wear was mainly performed on the ball. However, for the Al-DLC film with 11.04 at.% Al, it shows a deep and broad wear track, while its corresponding contact ball just exhibits a small wear scar, where the thick black transfer layer was observed. It can be said that the Al-DLC films were worn and a transfer layer was formed by materials detached from the films, which has been expected to account for the excellent friction per-formance [19,20]. As the Al concentration increases, the wear rate of the films increases and more materials were transferred from the films for the formation of the transfer layer. Accordingly, the friction coefficient of the films decreases with increasing Al concentration.

The graphitization of wear surface should be another important factor for the superior friction performance [21,22]. Fig. 8(e) presents the C 1 s spectra performed on the area around the wear track of the Al-DLC film (as shown in Fig. 8(b)). It could be seen that the FWHM of the C 1s peaks is larger than that of those C 1s spectra shown in Fig. 2. The C 1s XPS spectra can be also deconvoluted into two main peaks: sp^2–C around 284 eV and sp^3–C around 285 eV. Note that the peaks show higher sp^2/sp^3 ratio compared with those peaks in Fig. 2, and the peak at B area has the highest sp^2/sp^3 ratio among those spectra, which demonstrates that graphitization has occurred on the wear tracks.

4. Conclusions

Al-DLC films were deposited by a hybrid beams system comprising an anode-layer ion source and a magnetron sputtering unit. The Al concentration in the films was varied from 0.68 to 17.6 at.% as the sputtering current increased from 2 A to 3 A. The incorporated Al atoms were dissolved in the DLC matrix without bonding with C atoms, and the Al-DLC films exhibited an amorphous feature as the pure DLC film. Although both the internal stress and hardness decreased with increasing Al concentration, the internal stress dropped faster than the hardness. This indicates that we can acquire the DLC films with low internal stress and high hardness through Al incorporation. Furthermore, all Al-DLC films exhibited a lower friction coefficient compared with pure DLC film. The formation of transfer layer and the graphitization induced by friction were thought to account for the excellent friction performance.

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