Research Article

Tribological properties of platinum/ruthenium/nitrogen doped diamond-like carbon thin films deposited with different negative substrate biases

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Abstract: The platinum/ruthenium/nitrogen doped diamond-like carbon (PtRuN-DLC) thin films were deposited on Si substrates via DC magnetron sputtering by varying negative substrate bias. The tribological performance of the PtRuN-DLC films was systematically investigated using ball-on-disc microtribological test. The Raman results showed that the increased negative substrate bias significantly increased the number of sp\(^3\) bonds in the PtRuN-DLC films as a result of the increased kinetic energies of impinging ions. The adhesion strength of the PtRuN-DLC films apparently decreased with increased negative substrate bias due to the promoted residual stress in the films. The tribological results clearly revealed that the increased negative substrate bias decreased the friction and wear of the PtRuN-DLC films by improving the sp\(^3\) bonded cross-linking structures of the films. It can be concluded that the PtRuN-DLC films could effectively prevent their underlying Si substrates from wear as the negative substrate bias had a significant influence on the tribological properties of the PtRuN-DLC films.

Keywords: DC magnetron sputtering; PtRuN-DLC film; adhesion; friction; wear

1 Introduction

Diamond-like carbon (DLC) thin films are preferred as protective coatings for a number of tribological applications since they exhibit high hardness, high wear resistance, low friction and high corrosion resistance [1, 2]. Nowadays, the favorable surface smoothness of Si wafers encourages them to be applied in making microfluidic devices or secondary micromolds. However, the lifetime of Si micromolds has been significantly shortened by their high brittleness and friction. Recently, Saha et al. [3] reported that coating of Si micromolds with DLC films could successfully extend the lifetime of the micromolds.

The application of DLC films is greatly limited by their high residual stress because the poor adhesion strength of the DLC films associated with their high residual stress can result in their easy delamination in service [4–8]. The higher adhesion strength of DLC films can give rise to the better antiwear performance of the films without any significant adhesive failure in service. An introduction of an interlayer prior to DLC film deposition is a possible way to relax residual stress in the film [9]. Doping of metals, such as nickel (Ni), aluminum (Al) and so on, in DLC films promotes the adhesion strength of the films by relaxing the residual stress in the films with increased sp\(^2\) bonding in the films [10–13]. Khun et al. [8, 14, 15] found that doping of noble metals such as platinum (Pt) and ruthenium (Ru) improved the adhesion strength of DLC films because the metal induced graphitization of DLC films resulted in the relaxation of residual stress in the films. It was reported that doping of non-metals, such as nitrogen (N), etc., resulted in the enhanced adhesion strength of DLC films by increasing sp\(^2\) bonds and subsequently relaxing residual stress in the films [4, 5, 14, 16–18]. In addition, the tribological performance of DLC films can be improved by N...
doping because the incorporation of N in DLC films promotes the graphitization of the films and reduces the friction of the films via the enhanced lubricating effect [19–22]. It is expected that co-incorporation of Pt, Ru and N in DLC films could improve the adhesion strength and tribological performance of the PtRuN-DLC films for micromold applications.

It is known that the physical properties of DLC films greatly depend on the film deposition parameters, such as sputtering power, substrate bias, substrate temperature and so on. Substrate bias, which is an important parameter in magnetron sputtering deposition, influences the kinetic energy of impinging ions since the impinging ions with lower or higher kinetic energy than a penetration threshold result in sticking to the surface or penetrating into the surface to enter surface interstitial sites, respectively [4, 23]. The resulted changes in local density control the bonding structures of DLC films, which in turn affect the adhesion strength and tribological performance of the films. Khun et al. [6, 7] investigated the tribological properties of PtRuN-DLC films with respect to sputtering power and film thickness just to support the adhesion results of the films. However, the influence of substrate bias on the tribological properties of PtRuN-DLC films has not been reported yet. An understanding of a correlation between the negative substrate bias used during the deposition of PtRuN-DLC films and their tribological performance is necessary for successful micromold applications.

In this study, the PtRuN-DLC films were prepared on Si substrates via DC magnetron sputtering deposition by varying negative substrate bias from 0 to –120 V. The chemical compositions and bonding structures of the PtRuN-DLC films were measured using X-ray photoelectron (XPS) and micro-Raman spectroscopies. The adhesion strength of the PtRuN-DLC films was studied using micro-scratch test as the tribological properties of the PtRuN-DLC films were systematically investigated using ball-on-disc microtribological test.

2 Experimental details

The PtRuN-DLC films were fabricated on p-Si (111) substrates via DC magnetron sputtering deposition by varying negative substrate bias from 0 to –120 V. Prior to the film deposition, the Si substrates were ultrasonically cleaned with ethanol for 20 min followed by deionized (DI) water cleaning and air drying. Then, the Si substrates were placed in the deposition chamber for Ar plasma cleaning at a negative substrate bias of –250 V for 20 min to remove oxide layers on the substrate surfaces. All the film depositions were conducted by co-sputtering a graphite target (99.999% C) and a Pt/Ru alloy target (99.95%, Pt:Ru = 50:50) at DC powers of 700 and 15 W, respectively. During the film deposition, the substrate holder was held at a rotating speed of 10 rpm and at room temperature (about 22–24 °C) but the substrate temperature reached about 47 °C in maximum. The background and working pressures were 3.5 × 10⁻⁶ and 3 × 10⁻³ Torr, respectively. Ar (50 sccm) and N₂ (15 sccm) working gases were introduced together into the deposition chamber via mass flow controllers during the film deposition.

XPS (Kratos-Axis Ultra) was employed for elemental analysis. The pass energy was 160 eV for survey scans and 40 eV for detail scans of C 1s, N 1s and Pt 4f. The X-ray source used was monochromatic Al Kα line (hv = 1486.71 eV) with a power source of 10 mA × 15 KV.

The bonding structures of the PtRuN-DLC films were investigated using a confocal micro-Raman spectroscopy (Renishaw RM1000). A He–Ne laser with 632 nm line was used as an excitation source. An objective lens (×50) was used for a better signal to noise ratio. The Raman instrument had a spectral resolution of 1 cm⁻¹ and a spatial resolution of 1 μm.

The adhesion strength of the PtRuN-DLC films was evaluated using a micro-scratch tester (Shimadzu SST-101) with a diamond stylus of 15 μm in radius, which was dragged down on the films under progressive loading. The scan amplitude, frequency, scratch rate and down speed were set as 50 μm, 30 Hz, 10 μm/s, and 2 μm/s, respectively. Five measurements on each sample were conducted to get an average critical load.

Atomic force microscopy (AFM) (Digital Instrument, S-3000) with a tapping mode Si₃N₄ cantilever was used to measure the surface roughnesses of the PtRuN-DLC films in a scan size of 1 μm × 1 μm. An average surface roughness was determined from five measurements on each sample.
The tribological properties of the PtRuN-DLC films were investigated using a ball-on-disc micro-tribometer (CSM) by sliding against a Cr6 steel ball of 6 mm in diameter in a circular path of 1 mm in radius for about 10,000 laps at a sliding speed of 3 cm/s under a normal load of 1 N. Three measurements per sample were carried out to get an average friction coefficient. The width and depth of wear tracks were measured using a white light confocal imaging profilometry to get average wear width and depth with 4 measurements per wear track.

3 Results and discussion

The surface atomic percentages of N, C + Ru and Pt were obtained by integrating the core-level peaks of N 1s, C 1s + Ru 3d and Pt 4f and their atomic percentages are presented in Fig. 1 as a function of negative substrate bias. The N content decreases from about 22.96 to 20.62 at% while the C + Ru and Pt contents increase from about 76.62 to 78.70 at% and from about 0.42 to 0.68 at%, respectively, with increased negative substrate bias from 0 to –120 V. Since the kinetic energy of sputtered ions is proportional to substrate bias, the increased negative substrate bias accelerates the sputtered ions onto the film surfaces resulting in the proportionally increased C + Ru and Pt contents in the PtRuN-DLC films [24–28]. Compared to the ionization rate of N2 gas inside the deposition chamber, the increased kinetic energies of the C, Pt and Ru ions with increased negative substrate bias reduce the N content in the PtRuN-DLC films. In addition, the decreased N content can also be attributed to the reduced ionization process of N2 gas near the substrate to produce N ions during the film deposition with increased negative substrate bias. In the magnetron sputtering, the electrons that are ejected from the target surface are accelerated away from the cathode. These highly energetic electrons collide with atoms, creating ions. An unbalanced magnetron configuration used in this study escapes some electrons from the cathode region to ionize N2 gas in the plasma near the substrate for the sputtering deposition [23]. The increased negative substrate bias increases repulsion to those electrons, which partially degrades the ionization process of N2 gas so that the number of N ions reached to the substrate surface leads to decreasing as much as increasing the number of C, Pt and Ru ions with increased negative substrate bias.

Figure 2(a) shows the XPS C 1s + Ru 3d spectra of the PtRuN-DLC films as a function of negative substrate bias. The main peaks found at the higher binding energies are the overlapped C 1s and Ru 3d3/2 bands and the smaller peaks found at lower binding energies are Ru 3d5/2 bands. An unsymmetrical shape of the spectra becomes more significant with higher negative substrate bias due to the stronger C–C sp3 bonds. The increased negative substrate bias increases the kinetic energy of impinging ions, resulting in the increased content of sp3 bonds in the PtRuN-DLC films and the consequently increased bond disorder in the films [4, 29]. As a result, the full-width-at-half-maximum (FWHM) of the C1s peaks increases from about 2.82 to 2.95 eV with increased negative substrate bias from 0 to –120 V [30]. Normally, an introduction of N into an amorphous carbon structure tends to a decrease of sp3 bonding configuration because it encourages C to be in sp2 bonding configuration [31, 32]. It is therefore supposed that the decreased N content in the PtRuN-DLC films with increased negative substrate bias contributes to the increased formation of sp3 bonds in the films.

The N 1s spectra of the PtRuN-DLC films are presented in Fig. 2(b) as a function of negative substrate bias. The unsymmetrical shape of the N 1s peaks does not apparently change with increased negative substrate bias, which indicates that the introduced N atoms favor to exist in sp2 bonding configuration at the relatively high N content in the films [33–36]. However, the increased FWHM of the
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Fig. 2 XPS spectra of (a) C 1s + Ru 3d, (b) N 1s and (c) Pt 4f of PtRuN-DLC films as a function of substrate bias.

N 1s peaks with increased negative substrate bias reveals that the increased kinetic energy of imping ions promotes the disorder of N bonding configurations in the PtRuN-DLC films.

Figure 2(c) shows the Pt 4f spectra of the PtRuN-DLC films as a function of negative substrate bias. The PtRuN-DLC film deposited with the negative substrate bias of –120 V exhibits a larger broadening of the Pt 4f core level peak with a shift of about 0.4 eV to higher binding energy compared to the one deposited without the negative substrate bias probably due to the higher content of oxidized Pt species [37]. As a result, the FWHM of the Pt 4f peaks slightly increase from 1.54 to 1.64 eV with increased negative substrate bias from 0 to –120 V as found in Fig. 2(c).

The Raman spectra of the PtRuN-DLC films deposited with different negative substrate biases were fitted using Gaussian functions for both G and D peaks. Figure 3 illustrates the fitted Raman spectrum of the PtRuN-DLC film deposited with the negative substrate bias of –120 V, which reveals a typical DLC structure characterized by one band composed of G and D peaks. The G peak comes from the in-plane bond-stretching motion of pairs of sp² atoms without requiring the presence of sixfold ring so it comes from all sp² sites. D peak is due to a breathing mode of aromatic ring structures which only become active in the presence of disorder [29]. The significant appearance of the D peaks in the PtRuN-DLC films indicates the presence of high amount of aromatic rings in the films.

Figure 4 presents the Raman results of the PtRuN-DLC films deposited with different negative substrate biases. In Fig. 4(a), the G and D peaks of the PtRuN-DLC films decrease from about 1,552 and 1,387 cm⁻¹ to about 1,539 and 1,369 cm⁻¹, respectively, with increased negative substrate bias from 0 to –120 V. The increased sp³ bonds increase the bond disorder and the presence of nonsixfold rings, consequently softening their vibrational density and causing the downshifts in the both G and D peak positions [29]. Beeman et al. [38] revealed that the bond disorder and certain percentage of tetrahedral bonds could cause downshifts in both G and D peak positions. It is clear that the increased number of sp³ bonds in the PtRuN-DLC films with increased negative substrate bias is responsible for the downshifts in the both G and D peak positions.
because the increased kinetic energy of impinging ions promotes the energetic bombardment of the ions during the film deposition. The effect of noble metal content on the Raman shifts of the G and D peaks should be taken into account. Since Pt and Ru have higher atomic masses than C, doping of Pt and Ru increases the integrated atomic mass of the entire network resulting in a decrease of vibration frequencies of Raman active phases [39]. Therefore, the increased Pt and Ru contents in the PtRuN-DLC films with increased negative substrate bias (Fig. 1) tend to the downshifts in the both G and D peak positions (Fig. 4(a)).

In Fig. 4(b), the increased negative substrate bias from 0 to −120 V increases the FWHMs of the G and D peaks of the PtRuN-DLC films from about 174 and 370 cm$^{-1}$ to about 181 and 376 cm$^{-1}$, respectively, which is indicative of the increased bond disorder and distorted aromatic rings associated with the increased number of sp$^3$ bonds in the films [29, 40, 41]. In addition, the decreased N content in the PtRuN-DLC films with increased negative substrate bias (Fig. 1) is one of the reasons increasing the amorphization degree of the amorphous carbon structures through the decreased graphitization of the structures. Morrison et al. reported [42] that a decrease in the FWHM of G peak could be attributed to a decrease in residual stress within DLC film. Therefore, the increased FWHM of G peaks with increased negative substrate bias (Fig. 4(b)) indicates the development of residual stresses in the PtRuN-DLC films as a result of the improved sp$^3$ bonded cross-linking structures of the films.

The G peak is due to all sp$^2$ sites but the D peak is only due to aromatic rings [4]. Therefore, the decreased $I_D/I_G$ of the PtRuN-DLC films from about 1.52 to 1.35 with increased negative substrate bias from 0 to −120 V (Fig. 4(c)) is attributed to the decreased number of aromatic rings in the films. The decreased graphitization of the PtRuN-DLC films with decreased nitrogen content is one of the reasons decreasing the number of aromatic rings in the films with increased negative substrate bias. It is reported [11] that the introduction of metals into the amorphous carbon structure can promote sp$^2$ bonds via their catalytic effect. The metal phases can enhance the graphitization of amorphous carbon around them because the metal phases act as a catalyst during the energetic bombardment of impinging ions. Sputtering process can provide sufficient energy to locally heat the amorphous carbon on metal surfaces according to thermal spike model [43]. The substrate bias can also impart the higher kinetic energy of impinging ions. In addition, the amorphous carbon contacting with metal phases transforms to the graphite at relatively low temperatures [43–45]. Therefore, the metal-induced graphitization can cause a localized increase in sp$^2$ bonds in the amorphous carbon structure [43–45]. However, the increased Pt and Ru contents in the PtRuN-DLC films with increased negative substrate bias (Fig. 1) do not give rise to the increased graphitization of the films. The Raman results clearly show that the increased negative substrate bias significantly decreases the number of aromatic rings
in the PtRuN-DLC films so that the effects of Pt and Ru contents on the bonding structures of the PtRuN-DLC films in terms of metal-induced-graphitization are not significant in this study probably due to the relatively low Pt and Ru contents in the films and the stronger effect of energetic bombardment of impinging ions to form sp$^3$ bonds in the films.

Figure 5 shows the surface topographies of the PtRuN-DLC films deposited with different negative substrate biases. In Fig. 5(a), the PtRuN-DLC film deposited without negative substrate bias has the relatively rough surface topography with coarse asperities. However, the PtRuN-DLC film deposited with the negative substrate bias of –120 V has the much smoother surface topography with fine asperities as found in Fig. 5(b). At the high negative substrate bias of –120 V, the high energetic bombardment of impinging ions allows the penetration of the ions into the subsurface positions causing the local densification [4, 46]. In addition, the impinging ions penetrated into the subsurface positions dissipate their kinetic energies within thermal spike volumes, which induces the surface materials to be locally melted and consequently flattens the surface [47]. As a result, the PtRuN-DLC film deposited with the negative substrate bias of –120 V has the much smoother surface topography than the one deposited without the negative substrate bias, which is confirmed by the much smaller $R_a$ value (~0.16 nm) of the PtRuN-DLC film deposited with –120 V than that (~1.51 nm) of the one deposited without the negative substrate bias. The influence of N, Pt and Ru doping on the surface roughness of the PtRuN-DLC films should be taken into consideration. The N doping in DLC films can increase the surface roughness of the films because the increased number of sp$^2$ bonds and the aggregation of nitrogen inclusions in the films decrease the densification of the films [48]. Therefore, the decreased N content in the PtRuN-DLC films with increased negative substrate bias contributes to the reduced surface roughness of the films. The introduction of metals in DLC films can also increase the surface roughness of the films through the metal-induced graphitization and the aggregation of metal phases [49–51]. However, the increased Pt and Ru contents in the PtRuN-DLC films cannot be correlated to the decreased $R_a$ value of the films probably due to the relatively low Pt and Ru contents in the films.

The normal load at which a detachment of DLC film occurs is taken as a critical load to qualitatively measure the adhesion strength of the film since the magnitude of the critical load is related to the adhesion strength between the film and substrate [26]. It is known that the adhesion strength of DLC films is greatly influenced by the residual stress in the films [52–55]. The residual stress has two sources: thermal and intrinsic [52–55]. The difference in coefficients of thermal expansion (CTE) between DLC film and its substrate during cooling after the film deposition forms thermal stress in the film. Since the maximum substrate temperature reached during the PtRuN-DLC film deposition at RT is approximately 50 °C, the thermal stress is relatively quite low. The energetic bombardment of impinging ions during the

Fig. 5  AFM images showing surface topographies of PtRuN-DLC films deposited with substrate biases of (a) 0 and (b) –120 V.
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Film deposition can form intrinsic stress in DLC films by promoting the sp³-bonded cross-linking structures of the films with increased sp³ bonds [52–55]. In Fig. 6, the increased negative substrate bias from 0 to –120 V results in the decreased critical load of the PtRuN-DLC films from about 426 to 300 mN, which is indicative of the decreased adhesion strength of the PtRuN-DLC films because the increased number of sp³ bonds in the PtRuN-DLC films increases the residual stress in the films by promoting the sp³-bonded cross-linking structure of the films. It is reported [17, 18] that the incorporation of N in DLC films reduces the strain and subsequently releases the high residual stress in the films. Since the bond lengths of sp² bonds are shorter than those of sp³ bonds, the increased sp² bonds in the films with the incorporation of N reduce the strain in the films [17, 18]. In addition, C=O bonds that are shorter than C–C and C=C bonds also help to reduce the strain in the films [17, 18]. It is therefore supposed that the decreased N content in the PtRuN-DLC films with increased negative substrate bias contributes to the decreased critical load of the films as a result of the promoted residual stress in the films. The doped Pt/Ru can exist in the nitrogenated amorphous carbon matrix as undissolved Pt/Ru phases because their atomic diameters are much larger than that of C [36, 37]. The presence of the undissolved Pt/Ru phases in the matrix degrades the sp³-bonded cross-linking structure, resulting in the relaxation of residual stress. Therefore, the increased Pt and Ru contents with increased negative substrate bias (Fig. 1) should increase the critical load of the PtRuN-DLC films via the relaxed residual stress in the films. However, the decreased critical load of the PtRuN-DLC films with increased negative substrate bias (Fig. 6) clearly reveals that the effects of Pt and Ru contents on the critical load of the PtRuN-DLC films are not significant due to the relatively low Pt and Ru contents and the stronger influence of the negative substrate bias. It is clear that the increased negative substrate bias decreases the adhesion strength of the PtRuN-DLC films via the increased residual stress in the films.

The insets (bottom left and top right) in Fig. 6 show the scratch morphologies of the PtRuN-DLC films deposited with the negative substrate biases of 0 and –120 V, respectively, on which the film failures are found only at the relevant critical loads as a result of the relatively high cohesive strength of the PtRuN-DLC films [58–60]. The PtRuN-DLC film deposited with –120 V exhibits the more brittle fracture than the one deposited without negative substrate bias due to the much higher content of sp³ bonds in the film deposited with –120 V. Although the both PtRuN-DLC films are scratched under the same conditions, the PtRuN-DLC film deposited with –120 V possesses the wider scratch track than the one deposited without negative substrate bias since the much lower content of sp³ bonds in the PtRuN-DLC film deposited without negative substrate bias induces the higher interfacial shear strength between the diamond stylus and film and gives rise to a scratch track with smaller width by lowering the amplitude of vibrational motion of the diamond stylus during the scratch test [58–60].

Figure 7 shows the water contact angles of the PtRuN-DLC films deposited with different negative substrate biases. The increased water contact angle of the PtRuN-DLC films from about 59° to 71° with increased negative substrate bias from 0 to –120 V clearly indicates that the negative substrate bias used during the film deposition has a significant influence on the surface energy of the PtRuN-DLC films. It is known that the incorporation of N in the amorphous carbon structure decreases the water contact angle by increasing the surface energy because the strong polarity induced by carbon-nitrogen bonds causes polar-polar interaction with water molecules through electrostatic forces [16, 61]. Therefore, the decreased

Fig. 6 Critical loads of PtRuN-DLC films as a function of substrate bias. The insets show surface morphologies of scratched PtRuN-DLC films deposited with substrate biases of 0 (bottom left) and –120 V (top right).
N content in the PtRuN-DLC films with increased negative substrate bias results in the decreased polar component of the films and the subsequently increased water contact angle.

The tribological properties of the PtRuN-DLC films were investigated by sliding against a Cr6 steel ball for about 10,000 laps at a sliding speed of 3 cm/s under a normal load of 1 N and their friction results are presented in Fig. 8(a). The friction coefficient of the Si substrate slid against the Cr6 steel ball is 0.589 ± 0.001. Since a large contact between two contacting surfaces can give a high friction via an effective interfacial shear strength between them, the higher wear of the rubbing surfaces results in the higher friction via the larger contact between them [6, 7, 62]. Coating of the Si substrate with the PtRuN-DLC film deposited without negative substrate bias dramatically lowers the friction coefficient to about 0.301 because the PtRuN-DLC film effectively prevents the wear of the Si substrate and gives rise to the much smaller contact area between the rubbing surfaces [6, 7, 62]. In addition, the incorporation of N in the PtRuN-DLC film promotes the content of aromatic rings in the film and helps to lower the friction coefficient through the solid lubricating effect [6, 7, 62]. The increased negative substrate bias to –120 V further significantly decreases the friction coefficient of the PtRuN-DLC films to about 0.156 as found in Fig. 8(a) because the significantly increased number of sp³ bonds in the PtRuN-DLC films further reduces the contact area between the rubbing surfaces. Normally, the decreased content of aromatic rings in the PtRuN-DLC films with increased negative substrate bias (Fig. 4(c)) or decreased N content in the films (Fig. 1) should increase the friction of the films by reducing the solid lubricating effect of the films. However, the significantly decreased friction coefficient of the PtRuN-DLC films with increased negative substrate bias (Fig. 8(a)) clearly indicates that the solid lubricating effect of the PtRuN-DLC films on their friction is not significant because the significantly improved sp³-bonded cross-linking structures of the PtRuN-DLC films effectively not only prevent the direct contact between the steel ball and Si substrates via the high wear resistance of the films but also reduces the contact between the steel ball and films. The poor adhesion of the PtRuN-DLC films can give rise to a high friction by delaminating the films during the sliding and allowing the direct contact between the steel ball and Si substrates. However, no correlation between the decreased critical load (Fig. 6) and decreased friction (Fig. 8(a)) of the PtRuN-DLC films.
clearly points out that the adhesion strength of the PtRuN-DLC films is strong enough so that the increased wear resistance of the PtRuN-DLC films with increased negative substrate bias mainly contributes to the decreased friction of the films.

The surface roughness of the PtRuN-DLC films should be taken into account since a rougher surface can give a higher friction via mechanical interlocking between two mating surface asperities [7, 13, 62]. The increased negative substrate bias apparently decreases the surface roughness of the PtRuN-DLC films as shown in Fig. 5. It is clear that the decreased surface roughness of the PtRuN-DLC films contributes to the decreased friction of the films by weakening the mechanical interlocking between the two mating surface asperities.

The higher surface energy of the PtRuN-DLC films can give rise to the higher friction via the stronger attraction between two contacting surfaces [6, 7]. Therefore, the increased water contact angle of the PtRuN-DLC films with increased negative substrate bias (Fig. 7) clearly implies that the decreased surface energy of the PtRuN-DLC films is one of the reasons for the decreased friction of the films with increased negative substrate bias.

Fig. 8(b) illustrates the friction coefficients of the PtRuN-DLC films deposited with different negative substrate biases as a function of the number of laps. The sliding of the steel ball on the Si substrate exhibits the relatively high friction coefficient during the entire sliding. However, coating of the Si substrate with the PtRuN-DLC film deposited without negative substrate bias results in the dramatically decreased friction coefficient throughout the wear test as found in Fig. 8(b). In addition, the increased negative substrate bias further depresses the trends of friction coefficient versus laps of the PtRuN-DLC films as a result of the further decreased friction of the PtRuN-DLC films during the entire sliding. Although the Si substrate slid against the steel ball exhibits the stick-slip phenomenon, the presence of the harder PtRuN-DLC films on the Si substrates significantly suppresses the stick-slip phenomenon and gives rise to the relatively stable friction throughout the wear test. The results clearly show that the presence of the PtRuN-DLC films on the Si substrates dramatically reduces the friction by effectively preventing the wear of their underlying substrates.

The wear widths and depths of the PtRuN-DLC films deposited with different negative substrate biases are presented in Fig. 9. The wear width and depth of the Si substrate slid against the steel ball are about 457.3 ± 20 μm and 3,800 ± 42 nm. Coating of the Si substrate with the PtRuN-DLC film deposited without negative substrate bias dramatically decreases the wear width and depth to about 283 μm and 2225.7 nm as the wear width and depth of the PtRuN-DLC films further decrease from about 179.3 μm and 722.3 nm to about 97.9 μm and 194 nm with increased negative substrate bias from −30 to −120 V. It confirms that the PtRuN-DLC films can effectively prevent their underlying Si substrates from the wear. In addition, the improved wear resistance of the PtRuN-DLC films with increased negative substrate bias is responsible for the decreased friction of the films via the reduced contact between the steel ball and films.

After the tribological test, the wear morphologies of the Si substrate and PtRuN-DLC films deposited with different negative substrate biases were studied using scanning electron microscope (SEM). Figures 10(a) and 10(b) show the wear morphologies of the Si substrate observed at different magnifications, on which a significant wear track is found. As shown in Fig. 10(b), the localized removal of materials is apparently found in the center of the wear track of the Si substrate where the contact pressure is highest. During the wear test, the repeated sliding of the steel ball causes cyclic stress concentration in front of it, resulting in the surface fatigue which initiates minute
cracks in the subsurface and propagates them parallel to a free surface for some extent and eventually results in the localized removal of materials (Fig. 10(b)). However, coating of the Si substrates with the PtRuN-DLC films dramatically decreases the wear of the Si substrates as found in Figs. 10(c)–10(f), which confirms that the PtRuN-DLC films can effectively prevent their Si substrates from wear. Although the PtRuN-DLC film deposited without negative substrate bias prevents its underlying Si substrate from the severe surface wear and fatigue, the significant wear track on the surface of the PtRuN-DLC film (Figs. 10(c) and 10(d)) clearly indicates that the repeated sliding of the steel ball still can generate the surface wear of the PtRuN-DLC coated Si substrate. The much smaller wear track on the surface of the PtRuN-DLC film deposited with the negative substrate bias of −120 V (Figs. 10(e) and 10(f)) compared to that of the one deposited without negative substrate bias (Figs. 10(c) and 10(d)) clearly reveals that the higher negative substrate bias used during the film deposition gives rise to the much higher wear resistance of the PtRuN-DLC films through the higher content of sp³ bonds in the films.

4 Conclusions

The PtRuN-DLC films were prepared on the Si substrates via magnetron sputtering deposition by varying negative substrate bias. The tribological properties of the PtRuN-DLC films were systematically investigated. The Raman results showed that the increased negative substrate bias significantly increased the amount of sp³ bonds in the PtRuN-DLC films due to the increased kinetic energies of impinging ions. The critical load of the PtRuN-DLC films significantly decreased with increased negative substrate bias through the increased sp³ bonds in the films, which implied that the increased negative substrate bias decreased the adhesion strength of the PtRuN-DLC films. The tribological results clearly revealed that the PtRuN-DLC films effectively prevented their underlying Si substrates from surface wear and fatigue as the increased negative substrate bias significantly increased the wear resistance of the PtRuN-DLC films by improving the sp³-bonded cross-linking structures of the films. It can be concluded that the negative substrate bias used during the film deposition had a significant influence on the adhesion strength and wear resistance of the PtRuN-DLC films.

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