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The high-temperature tribological properties of Si-DLC films

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The tribological properties of Silicon-containing diamond-like-carbon (Si-DLC) films, deposited by magnetron sputtering Si target in methane/argon atmosphere, were studied in comparison with diamond-like-carbon (DLC) films. The DLC films disappeared because of the oxidation in the air at 500 °C, whereas the Si-DLC films still remained, implying that the addition of Si improved significantly the thermal stability of DLC films. Retarded hydrogen release from DLC film at high temperature and silicon oxide on the surface might have contributed to lower friction coefficient of the Si-DLC films both after annealing treatment and *in situ* high-temperature environment. Copyright © 2012 John Wiley & Sons, Ltd.

Keywords: silicon-containing diamond-like-carbon films; high-temperature tribology; thermal stability

Introduction

With the progress of size shrinkage and machining fine, mechanical systems are required to be run more efficiently in more harsh environments – such as high speed, high load, and extreme temperature, and radioactive and reactive atmospheres, which demand the moving parts possessing excellent properties, particularly, friction and wear resistance – to ensure the reliability of mechanical systems.[1] Diamond-like-carbon (DLC) films, due to their excellent properties, such as high hardness, low friction coefficient, high wear resistance, and chemical inertness,[2] have been believed as one of the ways to meet the referring challenges. DLC films are, however, easily oxidized at high temperature, resulting in the working lifetime decrease.[3–8] It has been reported that DLC films could remain stable at 400 °C and become graphitized above this temperature.[9,10]

Diamond-like-carbon films could attain to some extent high-temperature applications via doping with other elements.[11–14] Among those, the introduction of Si has been considered to improve the high-temperature tribological behavior or stability of DLC films. Hatada *et al.*[5] reported that with Si incorporation, the thermal stability and frictional property of DLC films have been improved at 500 °C because the chemical structure of the DLC films was modified and the graphitization could be prevented at higher temperature. The Si-DLC films with a silicon content of 11–21 at. % showed reasonable low friction coefficient and low wear rate, even after annealed at 500 °C, because of a thick silicon oxide layer with high thermal stability formed on the Si-DLC film during the sliding process.[6] Although the thermal stability and frictional property of the DLC films were improved with Si incorporation, a question is still there to be answered that whether there is any difference in tribological behaviors of DLC films doped with Si between annealed and in situ higher temperature. In this study, the tribological properties of Si-DLC films were investigated under both after annealing treatment and *in situ* high-temperature environment.

Experiment

The silicon-containing DLC films were deposited on silicon wafer substrates (N100) using a 20-kHz dual silicon target middle-frequency magnetron sputtering with a specific power of about 0.244 W/cm^2 (target size: 650 mm × 72 mm × 6 mm). The substrates were ultrasonically cleaned with acetone before their introduction into the deposition chamber. The base pressure before deposition in the chamber was 3×10^{-4} Pa, and then, the substrates were cleaned again by argon ion bombardment with a substrate bias at −1000 V for 15 min, in order to remove the surface native oxide. The films were deposited with a high-purity pyrolytic silicon target (99.99%) as silicon source. The mixture gases of methane (CH_4) and argon (Ar) were introduced into the vacuum chamber; the film composition was altered by varying the flow rates of the CH_4 and Ar gases. When the mixed gases were fed into the vacuum chamber, the base pressure of the vacuum chamber was 4–7 Pa. A negative DC voltage bias of −0.4 kV was applied to the substrate. The thermal stability investigation of the as-deposited films was carried out in a furnace under atmosphere for 0.5 h with temperatures ranging from 200 to 500 °C.

The thicknesses of the film were measured by cross-sectional scanning electron microscopy (SEM) observation. Raman spectrometer of all samples was measured by a micro-Raman with a LABRAM HR 800 micro-spectrometer at a wavelength of 532 nm (2.3 eV). The chemical composition and bonding structure of the films were determined by a PHI-5702 multifunctional X-ray photoelectron spectroscopy (XPS) under Mg Kα X-ray irradiation; Fourier transform infrared (FTIR) spectra of Si-DLC films were recorded on an IFS66V/S spectrometer to detect the changes of the bonding structure in the films. The friction behaviors were evaluated on a commercial reciprocating ball-on-disc tribometer (CSM TRIBOMETER, Switzerland) was utilized to perform sliding tests on both films from room temperature to 400 °C, against

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Al_2O_3 ceramic ball with a diameter of 6 mm. A constant load of 2 N, a rotation speed of 85 r.p.m., a rotation diameter of 10 mm, and a range of 1000 cycles were maintained in all tests; the relative humidity is 30–40%; the annealed films obtain the friction coefficient at some friction conditions and at room temperature.

Results and discussion

Structure and composition of the DLC films

The thicknesses of the films gauged by cross-sectional SEM are shown in Table 1. The deposition rate of the films and the silicon content of Si-DLC films both increased with increasing the Ar fraction in the mixed gases, determined by XPS.

After deposition, all films were annealed at different temperatures ranging from 200 to 500 °C, to determine the thermal stability. The results proved that DLC films exfoliated and disappeared at 500 °C because of the oxidation in the air; Si-DLC films, however, still remained after disposed at 500 °C. Detailed study of the intrinsic factors endows the better tolerance to Si-DLC films are discussed as follows.

Raman spectrum is used to probe the bonding characters of carbon-based films. There is a typical character of DLC films in the region of 1000–1800 cm^{-1}:a G peak around 1560–1600 cm^{-1}, originated from optical zone center vibrations (E_{2g} mode) of all pairs of sp^2 C atoms in aromatic rings and olefinic chains, and a D shoulder peak, around 1350 cm^{-1} attributed to the breathing modes of sp^2 atoms in clusters of sixfold aromatic rings, respectively.[15] The intensity ratio, ID/IG ratio, is considered as the indicative of the cluster size and the degree of order in the clustered aromatic sp^2 phase of carbon films.[16,17] Figure 1(a) shows the Raman spectra acquired from DLC films before and after annealed at different temperatures. After annealing, clearly, the D peak became apparent, ID/IG increased from 1.8 to 2.5, and the G peak position shifted from 1561 to 1574 cm^{-1}, which can be attributed to the structure change of the films that more and large graphitic clusters or layers were induced by annealing.[18,19] In contrast, the peak shapes of the Si-DLC films are nearly unchanged even annealed at 500 °C, as shown in Fig. 1(b) and(c). The D band became more intense for the 16 at. % Si-DLC film after being annealed at 500 °C, whereas almost unchanged for the 26 at. % Si-DLC films. However, the value of ID/IG decreases from 1.5 to 1.0, and the G peak position shifted from 1530 to 1524 cm^{-1}, for the 26 at. % Si-DLC film with increasing annealing temperature; this is known to be related to the increase of the sp^3 hybridized bonds of carbon.[6] The slope of the base line of the Raman spectra increased with increasing annealing temperature (Fig. 1) owing to the formation of Si–O bonds in the films, which strengthens fluorescence emission of the Ar ion laser.[5]

Figure 2 shows XPS spectra of C1s for the DLC, the 16 at. % Si-DLC and 26 at. % Si-DLC treated at different annealing temperature. With the increase of annealing temperature under air condition, the peak shifted from 284.5 to 285 eV, implying that the extent of the film oxidation increased.

Figure 3 shows Si2p XPS spectra of Si-DLC films that Si presented in the form of SiC in the fabricated film and retained the same status even after annealed at 200 °C. Up to the annealing temperature at 400 °C, the SiC in Si-DLC film with 16 at. % Si was oxidized to SiO_2. However, the oxidation of SiC in the Si-DLC film with 26 at. %

Table 1. Deposition parameters of DLC and Si-DLC films

	Ar flow rate (sccm)	CH_4 flow rate (sccm)	Thickness (μm)	Deposition rate (μm/h)
(a) DLC	100	200	3.0	2.0
(b) Si-DLC	100	200	3.6	2.4
(c) Si-DLC	150	200	3.9	2.6

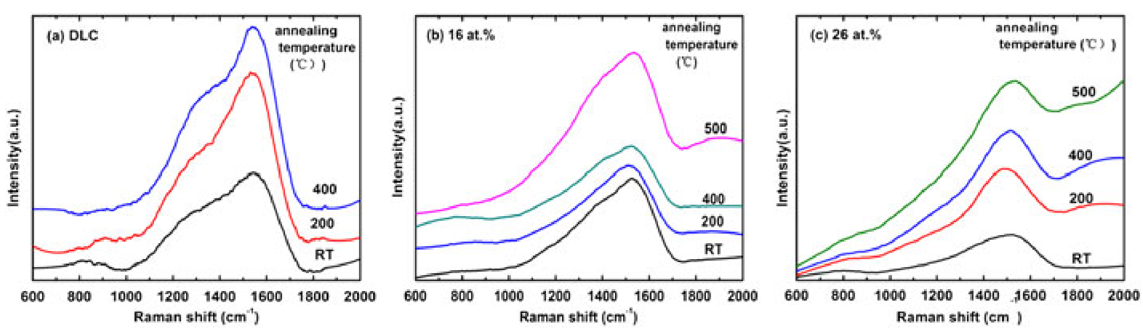

Figure 1. Raman spectra of annealed (a) DLC, (b) Si-DLC (16 at. %), and (c) Si-DLC (26 at. %) films.

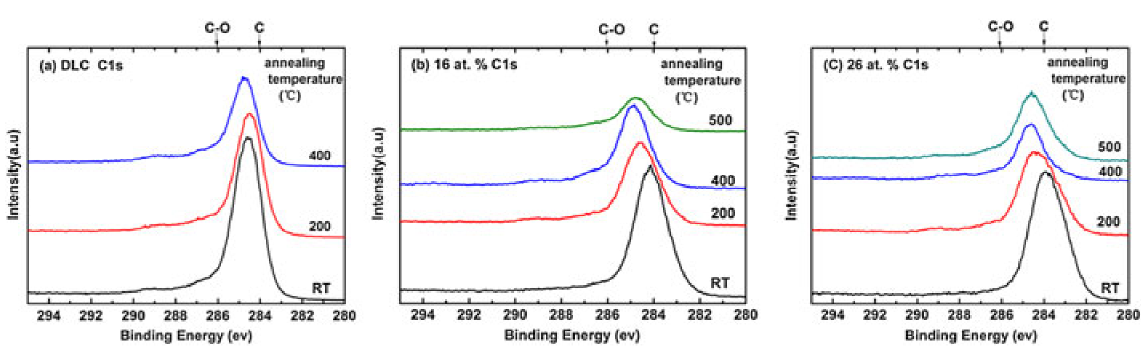

Figure 2. XPS C1s of annealed (a) DLC, (b) Si-DLC (16 at. %), and (c) Si-DLC (26 at. %) films.

Si was not completed at 400 °C; the full oxidation temperature was increased from 400 to 500 °C, compared with Si-DLC film with 16 at. This definitely indicated that the addition of Si improved the thermal stability of DLC film, and the higher Si content introduced the higher thermal stability. With a further increase in the Si content to 29 at.%, the film shows an amorphous SiC-like characteristic; that is, some cracks are observed on the film surfaces after sliding, which results in a high friction.[6]

Figure 4 shows the FTIR of DLC films and Si-DLC films with different annealing temperatures. Generally, the analysis of FTIR spectra of amorphous carbon films is according to the pioneering work of Kaufman *et al.*[20] The peaks in the range of 2675–3250 cm^{-1} are attributed to the different stretching vibrations of C–H bonds. The Si–H bands are arising at 2025–2250 cm^{-1}. The Si–C bonding was observed at 700–800 cm^{-1} along with a broad band between 900 and 1000 cm^{-1} attributed to the different shear vibrations of Si–CH bonds. Dillon *et al.*[10] found that the hydrogen of the DLC films began to overflow at 100 °C in the air, and at 400 °C, the hydrogen overflowed completely. In this study, it is obvious that the C–H bonds of DLC films become weaker and disappear after annealing. However, the C–H bonds of Si-DLC films are almost unchanged after annealing up to 400 °C. Interestingly, the C–H peak of the 16 at. % Si-DLC film almost disappeared, whereas that of the 26 at. % Si-DLC film did not changed significantly after annealing at 500 °C. Comparing the three samples, one can deduce that Si might replace H to form Si–C causing the reduction of the adjacent C–H bonds and difficulty in exhalation of H_2 molecules.

Friction properties

The friction coefficients of the DLC films and Si-DLC films sliding against Al_2O_3 ceramic ball with diameter of 6 mm under constant normal load of 2 N and a relative humidity of 30–40% in the air are presented in Fig. 5. The value of the coefficient is an average of at the sliding time of 1800 s. After annealing at 400 °C, the friction coefficient of the DLC films obviously increased from 0.13 to 0.24; it might be attributed to the heavy oxidation of the DLC film. In contrast, the Si-DLC films show lower friction coefficient after annealed, probably because of the formation of silicon oxide on the film surface,[5] confirmed in Fig. 3, but SiO_2 does not have intrinsic low friction; therefore, the reason might be attributed to unique surface structure of the film that silicon oxide embedded in DLC; however, the real and deep understanding of the SiO_2 role in lowering friction is still unrevealed; more

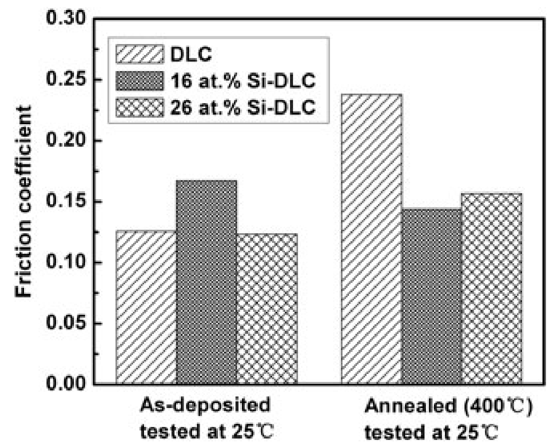

Figure 5. Friction coefficients of DLC films, 16 at. % Si-DLC films and 26 at. %Si-DLC films before and after annealed at 400 °C for 30 min.

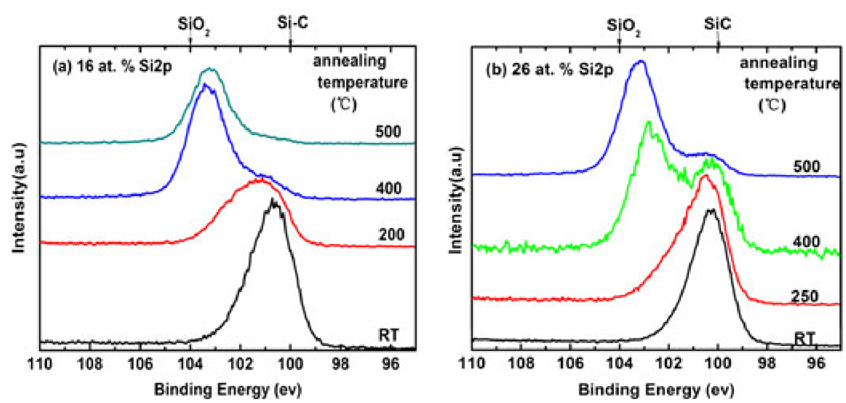

Figure 3. XPS Si2p of annealed (a) Si-DLC (16 at. %), and (b) Si-DLC (26 at. %) films.

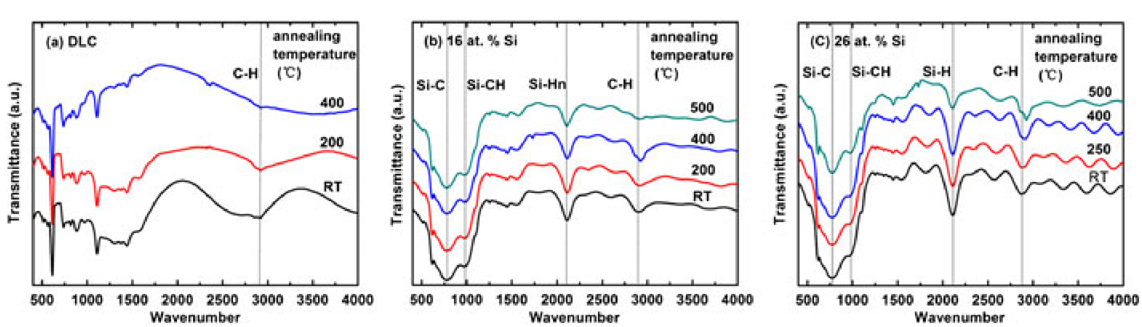

Figure 4. FTIR of annealed (a) DLC, (b) Si-DLC (16 at. %), and (c) Si-DLC (26 at. %) films.

systematical investigation is necessary in the future. The 16 at. % Si-DLC film shows lower friction coefficient after annealing, but the 26 at. % Si-DLC film shows higher friction coefficient because of high content of amorphous SiC-like characteristic.[6] As shown in Fig. 3, the Si-DLC film with 16 at. % Si was oxidized to SiO_2 after annealed at 400 °C; however, for the 26 at. % Si-DLC film, the oxidation of SiC was not completed. As we have known, the amorphous SiC-like characteristic results in high friction. The value of ID/IG decreases for the 26 at. % Si-DLC films with increasing the annealing temperature, so the content of the sp^3 increase, which results in a high internal stress, provided a high friction.

It is verified that the addition of Si improved the thermal stability and frictional behavior even after annealing, whereas it is different from *in situ* high-temperature environment. In order to further investigate the influence of temperature on the friction properties, the friction coefficient of DLC films and Si-DLC films have been carried out under *in situ* higher temperature from room temperature to 400 °C in the air (Fig. 6). The friction coefficient of the DLC films at room temperature was 0.15, whereas the friction coefficients of the Si-DLC films were 0.17 and 0.12 for Si content of about 16 at. % and 26 at. %, respectively. Obviously, the introduction of Si did not lower the friction coefficient of DLC film; inversely, it led to higher friction. As the testing temperatures increased to 200 °C, the friction coefficient of the DLC films, 16 at. % and 26 at. % Si-DLC films, are decreased to 0.06, 0.09 and 0.10, respectively. All three samples demonstrated lower friction compared with the results in room temperature, probably, because of the fact that partial amorphous transformed to graphite-like structure induced by annealing effect (verified in Fig. 1(a)). The abrupt change of the friction coefficient occurred at the temperature of 400 °C for the DLC films that increased to 0.3; because of the hydrogen overflow, hydrogen is believed to be of benefit to the lower friction coefficient of DLC film, and oxidation damage. Interestingly, the friction coefficient of Si-DLC films has little change with increasing temperature.

As discussed earlier, the Si introduction improved the thermal stability of DLC film, and silicon oxide would form on the DLC surface, which suppressed further oxygen diffusion into DLC film to retard the oxidation of DLC film at higher temperature. There is no obvious change in C–H intensity after annealed, as shown in Fig. 4(b) and (c); this indicated that the hydrogen retainment in carbon matrix might be the key factor to the lower friction of Si-DLC films at high temperature.

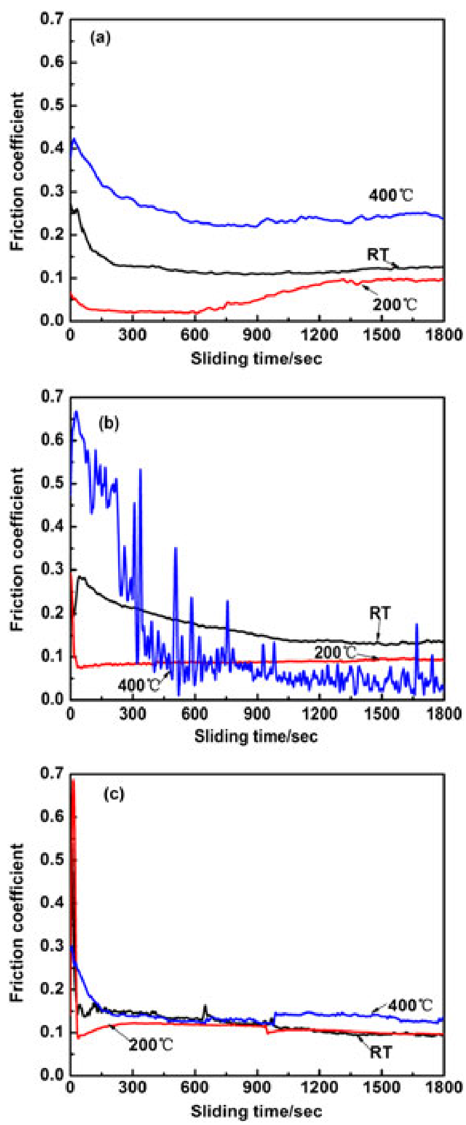

Figure 6. In situ high-temperature friction coefficient of (a) DLC, (b) Si-DLC(16 at. %)and (c) Si-DLC (26 at. %) films.

Conclusion

The DLC films disappeared because of oxidation in the air after annealing, whereas the Si-DLC films still remained until 500 °C. Si-DLC films possess lower friction coefficients, both after annealing treatment and *in situ* high-temperature environment. The introduction of Si into the DLC film improved the thermal stability and suppressed oxidation, and retarded hydrogen release from DLC film at high temperature and silicon oxide on the surface of the Si-DLC films might contribute to lower friction coefficient both after annealing treatment and *in situ* high-temperature environment.

Acknowledgements

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