Applied Surface Science 258 (2012) 5025–5030

Contents lists available at SciVerse ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Mechanical and tribological properties of Ti-DLC films with different Ti content by magnetron sputtering technique

Jinfeng Cui[a], Li Qiang[a,b], Bin Zhang[b], Xiao Ling[a,b], Tao Yang[a,b], Junyan Zhang[b,*]

[a] School of Petroleum Chemical Engineering, Lanzhou University of Technology, Lanzhou 730050, PR China
[b] State Key Laboratory of Solid Lubrication, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, PR China

ARTICLE INFO

Article history:
Received 28 November 2011
Received in revised form 10 January 2012
Accepted 12 January 2012
Available online 31 January 2012

Keywords:
Diamond-like carbon film
Different concentration Ti doping
Low concentration Ti doping
Mechanical properties
Tribological performance

ABSTRACT

Ti-doped diamond-like carbon (DLC) films were deposited on Si substrates at room temperature by magnetron sputtering Ti twin-target in methane and argon mixture atmosphere. The DLC films with different Ti concentrations were fabricated by varying the gas flow ratio of Ar/CH_4. X-ray photoelectron spectroscopy (XPS), Raman spectra were used to analyze the composition and the microstructure of the films. The internal stress was calculated by using the Stoney equation, where the curvature of the film/substrate was measured by BGS 6341 type film stress tester. The mechanical and tribological properties of the films were systematically studied by the nano-indentor and reciprocating ball-on-disc tester, respectively. The Ti atomic concentration in the films increased from 0.41% to 8.2% as the Ar/CH_4 flow ratio increased from 60/190 to 140/110. The Ti atoms exist mainly in the form of metallic-like Ti rather than TiC when Ti concentration is 0.41%, confirmed by XPS analysis. As the Ti concentration rose to 6.7%, the Ti-DLC films transformed to composite DLC films with carbide phase embedded in the DLC matrix because of the formation of TiC. As a result, the hardness is decreased, while the stress is dramatically increased. The Ti-DLC films with 0.41% Ti doping showed a relatively high hardness (13.75 GPa), low stress (0.56 GPa), extremely low wear rate ($\sim10^{-10}$ mm^3/Nm) and low friction coefficient (0.05).
© 2012 Elsevier B.V. All rights reserved.

1. Introduction

Metal-doped diamond-like carbon (DLC) films have attracted more and more attention in the area of science due to promising properties such as high hardness, low friction coefficient and residual stress, high wear-resistance [1,2]. Numerous metal elements (including Ti, Cr, Ni, W, Al, etc.) have been used to improve the properties of the films [3–10]. However, many studies suggested that the metal incorporated into carbon matrix may form nanoclusters or MeC microstructure by bonding with carbon atoms as long as the concentration of doped metal is high enough, these nanoclusters or MeC microstructures would break up the continuity of the carbon network and thus resulting in the decrease in the films hardness [4,11]. Moreover, amorphous Me–C phase might be formed at high concentration metallic doping, leading to the increase in residual stress [12–14].

Therefore, it is possible and feasible to fabricate Me-DLC films with relatively high hardness and low residual stress with low concentration metal doping because MeC nanoparticles could not form at low metal concentration, and thus lowering residual stress and at the same time retaining the high hardness of DLC film. Using a hybrid linear ion beam system, Dai and Wang [15] investigated the low Cr concentration doped DLC films, and found that the residual stress of the films showed a significant reduction, while the hardness of the films still retained a high value. The results from Meng and Gillispie [16] also suggested that there was no obvious reduction in the hardness of the films when the doped Ti content in DLC film was down to low level.

In this study, different concentration Ti-containing hydrogenated DLC films were deposited by magnetron sputtering Ti twin-target via varying the gas flow ratio of Ar/CH_4. The purpose of this study is to get a better understanding of the excellent performance of low concentration Ti-containing DLC films by comparing with different Ti concentration. Thus, it will be of help to the fabrication of Me-DLC films with excellent friction and wear performance for a wide range of tribological application. Although the low concentration Ti-doped DLC films have been reported, the studies about this aspect are still necessary because it is a long time to realize its industrial application. Therefore, mechanical properties and tribological performances of the films were investigated systematically, the result indicates the films with relative high hardness and elastic modulus, low residual stress, excellent wear-resistance performance could be obtained via a low concentration Ti doping.

* Corresponding author. Tel.: +86 0931 4968295.
E-mail address: zhangjunyan@licp.cas.cn (J. Zhang).

0169-4332/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
doi:10.1016/j.apsusc.2012.01.072

2. Experimental procedure

2.1. Films deposition

Different concentration Ti-doped DLC films were deposited by magnetron sputtering system consisting of DC magnetron sputtering with 15 mm (W) × 672 mm (L) rectangular Ti twin targets (99.99% purity). The volume of the vacuum chamber was 0.8 m^3. A n-type Si (1 0 0) wafer with a thickness of 625 ± 10 μm was used as the substrate. All the substrates were ultrasonically pre-cleaned with acetone and then ethanol rinsed in deionized water in order to remove the grease contamination, dried in the ambient atmosphere before being put into the chamber. Prior to the deposition, the vacuum chamber was evacuated up to 1.0×10^{-3} Pa, and then 200 sccm argon was introduced into the chamber. All substrates were sputter-cleaned by an argon discharge for 30 min at a bias voltage of −1200 V in order to remove surface oxide contamination. During films deposition, CH_4 and Ar mixture, 250 sccm total gas flow, was supplied to the sputtering source as the working pressure. The power of the sputtering source was about 5.6 kW (∼560 V, 10 A). Ti concentration was controlled by varying the gas flux ratio of Ar/CH_4, the working pressure was kept at a constant value of about 0.7 Pa through a pressure valve. A negative pulsed bias voltage of 1600 V was supplied to the substrate during the films deposition. The deposition time was kept at about 60 min for all the samples. After processing, the substrate was cooled down to room temperature inside the chamber in an argon atmosphere. Furthermore, the pure DLC films were prepared at the Ar/CH_4 ratio of 0/250 for comparison. In the further text, sometimes the terms "DLC, Ti-DLC-1, Ti-DLC-2, Ti-DLC-3" were used to denote the films with 0%, 0.41%, 6.72% and 8.2% Ti concentration, respectively.

2.2. Sample characterization

The thickness of the DLC films was measured by cross-section SEM images (Hitachi S-4800). The chemical composition of the films was determined by a PHI-5702 multifunctional X-ray photoelectron spectroscopy (XPS, ESCALAB 210), with Al Kα radiation (photo energy 1476.6 eV) as the excitation source. The energy analyzer was set such that the Au ($4f_{7/2}$) line was recorded as reference with a full width at half maximum of 0.9 eV. The mechanical properties were measured by nanoindenter (Nano inderter II, MTS Co. Ltd. of America) with a maximum indentation depth of 50 nm in order to avoid the influence of substrate. The internal stress was calculated from the curvature of film/substrate using the Stoney equation, and the curvature of the film/substrate was measured by BGS 6341 type film stress tester. The tribological behaviors of the Ti-DLC films were investigated with a reciprocating ball-on-disc tester, which slide at 23 °C and at relative humidity (RH) of 30% under dry sliding conditions; Al_2O_3 (5 mm in diameter) was used as the mating material. All the tests were performed at 10 cm/s sliding velocity and the applied load was 10 N. After testing, the total volume of wear scar was calculated from at least five measurements by a surface three-dimensional profiler, and then the specific wear rates of the films were defined as the volume of removed material at an unit load and in an unit sliding distance (mm^3/Nm). The specific friction coefficient and wear rate were calculated by averaging the data of at least 5 individual operations. All mentioned friction coefficient and wear rate refers to the mean friction coefficient and wear rate in this paper.

3. Results and discussion

3.1. Ti concentration and film growth rate

Fig. 1 shows the Ti concentration and the average growth rate of the films as a function of the Ar/CH_4 flow ratio. It is noticeable that

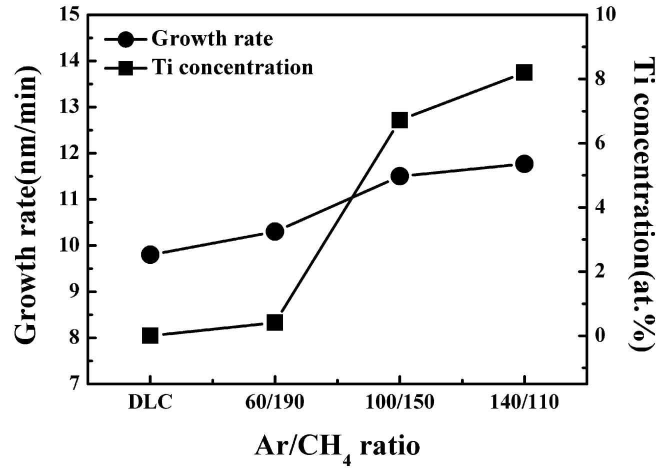

Fig. 1. The film growth rate and Ti concentration as a function of the Ar/CH_4 flow ratio.

both the Ti concentration and growth rate increase with increasing Ar/CH_4 flow ratio. As the Ar/CH_4 flow ratio increases from 0/250 to 140/110, the Ti concentration increases from 0 to 8.2%, which indicates the Ti concentration can be adjusted by changing the Ar/CH_4 flow ratio. Meanwhile, the growth rate increases from 9.8 nm/min to 11.77 nm/min, which indicates the growth rate could be improved by changing the Ar/CH_4 flow ratio. The dynamic balance between the film growth and cleaning on target surface could be used to explain this phenomenon. At relatively high Ar/CH_4 flow ratio, the ionization rate of CH_4 gas increases because of the collision of large amount of Ar^+ ion and CH_4 gas, which causes the growth rate increases. Furthermore, the target surface collision with Ar^+ ions is so strong that large amount of Ti atoms can be easily sputtered out, which causes the increase in Ti concentration. As the Ar/CH_4 flow ratio decreases to 60/190, the target surface has been almost completely covered by carbon from ionized CH_4, this is so-called "target poisoning", which causes the decrease in Ti concentration.

3.2. XPS analysis

The bonding natures of samples were investigated using XPS analysis. Fig. 2 presents the XPS C 1s spectra of the Ti-DLC films with

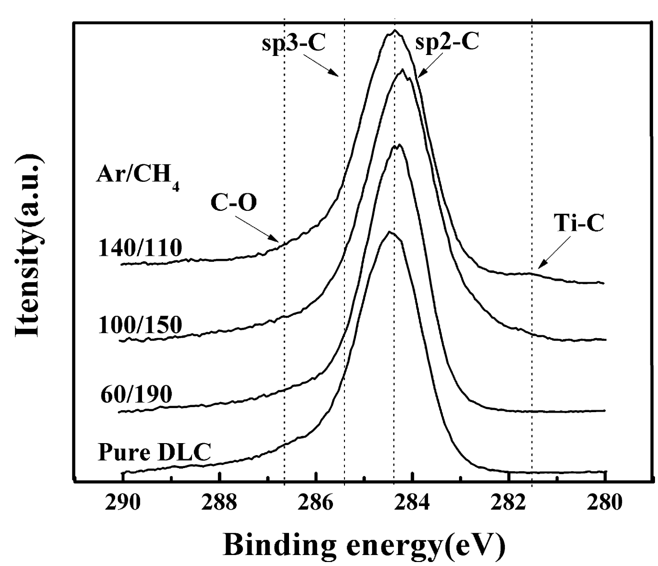

Fig. 2. The XPS C 1s peak of the films deposited at the different Ar/CH_4 flow ratios.

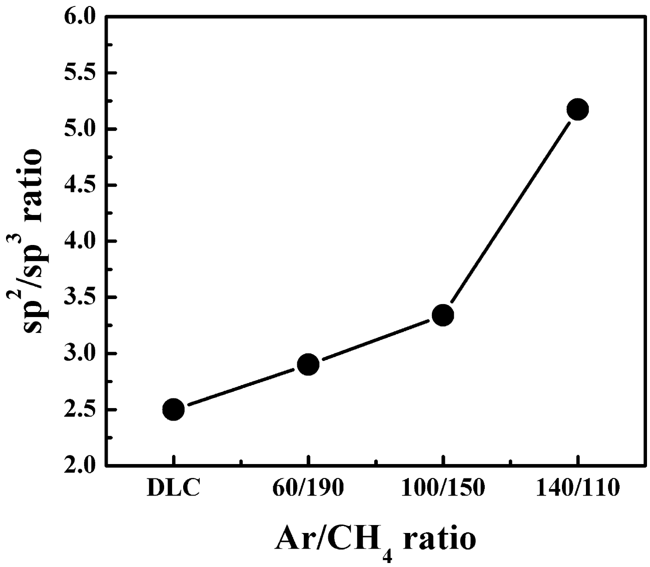

Fig. 3. The sp^2/sp^3 ratio as a function of the Ar/CH_4 flow ratio.

different Ar/CH_4 flow ratio. A major peak around 284.5 eV, representing the typical binding energy of the DLC films, was observed. Generally speaking, the C 1s core peak can be deconvoluted into three Gaussian peaks around 281.9 eV, 284.4 eV and 285.2 eV. The peak around 281.9 eV is assigned to Ti—C bonds [17], the peak around 284.5 eV and 285.2 eV are assigned to sp^2 and sp^3 bonded carbon atoms [18], respectively. Subsequently, the sp^2/sp^3 ratio is measured by taking the ratio of the sp^2 peak area over the sp^3 peak area. Fig. 3 displays the sp^2/sp^3 ratio as a function of the Ar/CH_4 flow ratio. It is obvious that the sp^2/sp^3 ratio increases monotonically with the increase in the Ar/CH_4 flow ratio. The sp^2/sp^3 ratio is 2.5 for the pure DLC and 5.175 for Ti-DLC-3, which implies an increase in sp^2 content. This indicates the Ti incorporation induced the transformation of sp^3 to sp^2, that means the film became more graphite like. However, the peak around 281.9 eV, corresponding to Ti—C bonds, could not be found for the film with Ti concentration of 0.41%, deposited at 60/190, which indicates the Ti incorporated into the carbon matrix does not bond with the carbon atoms. When the Ar/CH_4 flow ratio increases to 100/150, the shoulder peak around 281.9 eV appeared. This demonstrates that the carbide is formed in the films as the Ti concentration increases to 6.72%. The detected C—O bonds might be attributed to the contamination when the sample is exposed to the air [19]. At the same time, it should be noted that the C—O peak area is so small that it hardly can be discerned. This might be assigned to the low oxygen concentration (not shown here).

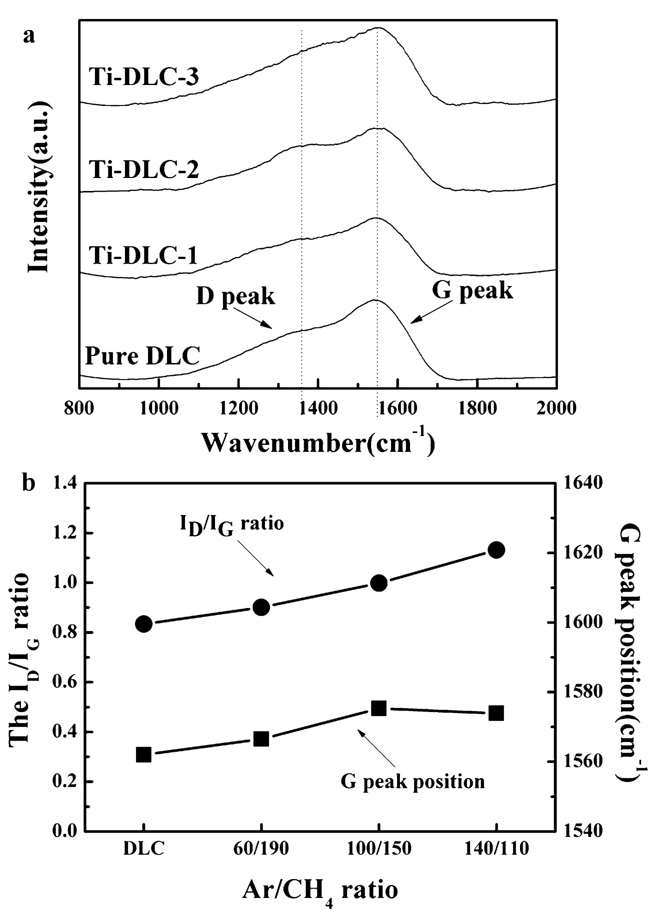

Fig. 4. (a) Raman spectra and (b) the corresponding G-peak position and I_D/I_G ratio of the Ti-DLC films deposited at different Ar/CH_4 flow ratio.

3.3. Raman analysis

Raman spectroscopy is generally used to obtain the detailed bonding structure of the DLC films. Fig. 4(a) displays the typical Raman spectra of the films deposited at different Ar/CH_4 flow ratios

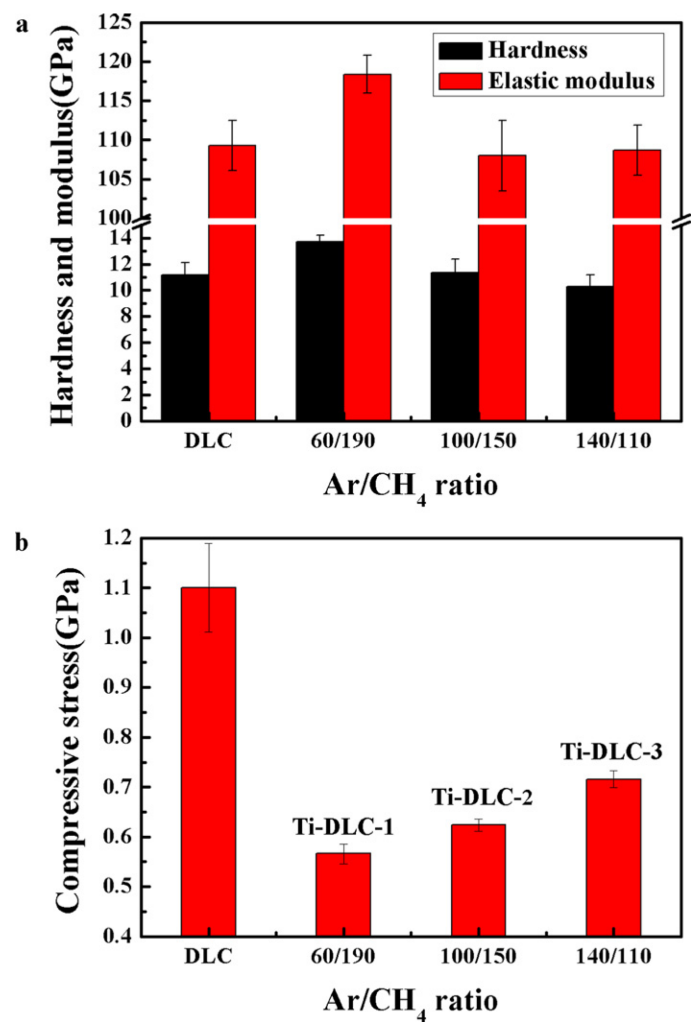

Fig. 5. (a) Hardness, elastic modulus and (b) compressive stress as a function of the Ar/CH_4 flow ratio.

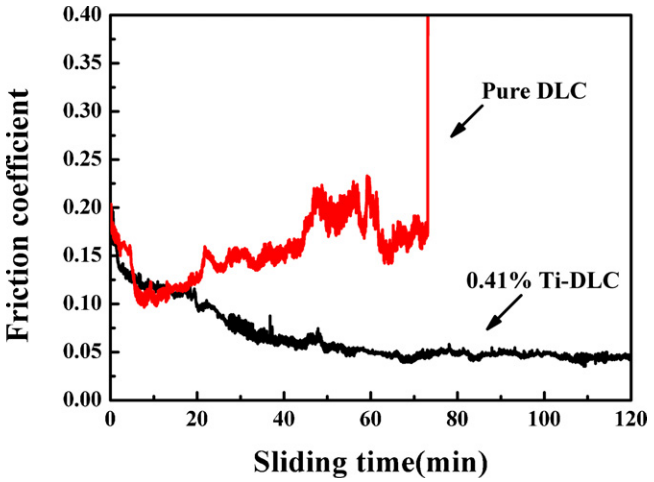

Fig. 6. Comparisons of friction behaviors between low concentration Ti-doped DLC film and pure DLC film. Testing condition: load, 10 N; counterparts: Al_2O_3 balls (5 mm); sliding velocity: 10 cm/s; relative humidity: 30%; room temperature.

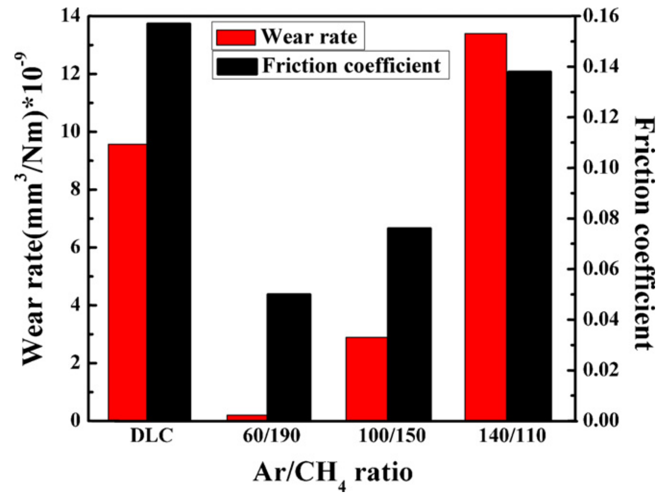

Fig. 8. The average friction coefficient and wear rate of the films deposited at different Ar/CH_4 flow ratio.

in the wavelength range of 800–2000 cm^{-1}. A broad peak at approximately 1560 cm^{-1} and an obvious shoulder peak, which represents the typical characteristic of hydrogenated amorphous DLC films, could be observed. Generally, the Raman spectra can be fitted by the two Gaussian peaks at about 1580 cm^{-1} (labeled as 'G' peak) and 1350 cm^{-1} (labeled as 'D' peak)[20]. The G peak is due to the bond stretching of sp^2 atoms in both aromatic rings and chains, while the D peak is attribute to the breathing modes of sp^2 atoms only in aromatic rings [12]. The sp^2/sp^3 ratio can be characterized by the G peak position and the relative ratio of the D peak to G peak (I_D/I_G). Normally, the G peak position and I_D/I_G ratio increase with the increasing of sp^2/sp^3 ratio in hydrogenated amorphous DLC films [4]. The G peak position and I_D/I_G ratio of the films as a function of the Ar/CH_4 ratio are shown in Fig. 4(b), it should be noted that the G peak position and I_D/I_G ratio increase monotonically with increasing Ar/CH_4 flow ratio, which indicates that the sp^2/sp^3 ratio increases with the Ar/CH_4 flow ratio, consistent with the XPS analysis. At the low Ti doping level, Ti does not bond with the carbon atoms but causes the distortion of bond angles. As a result, the films tend to be graphitized. As the Ti concentration increases, the compressed carbon (sp^3) network reduces, because the formation of TiC may damage the carbon three-dimensional network in the DLC.

3.4. Internal stress and hardness

Fig. 5 displays the internal stress, hardness and elastic modulus of the films as a function of the Ar/CH_4 flow ratio. The internal stresses of all samples have compressive stress. Furthermore, the stress dramatically decreases from 1.1 GPa to 0.56 GPa as the Ar/CH_4 flow ratio increases from 0 to 60/190. As the Ar/CH_4 flow ratio increases further, the internal stress increases. Wang et al. [13] investigated the stress behavior of W-incorporated hydrogenated amorphous carbon films, and found that the internal stress could be relaxed sharply due to the distorted bonds at low concentration metal doping. Obviously, the internal stress is relaxed at initial stage, which may attribute to the distortion of bonds at low concentration Ti doping. As the Ar/CH_4 flow ratio increases further, the amorphous TiC phase is formed, confirmed by XPS analysis. The Ti—C bonds, longer bond length than C—C bonds, would cause the internal stress increases. However, the hardness of the films with low concentration Ti doping is higher than the pure DLC films, which may be attributed to the solid solution hardening effect [3]. As the Ar/CH_4 flow ratio increases further, the hardness decreases dramatically. One main factor should be considered that the formation of TiC phase may break the continuity of carbon network, thus resulting in the decrease in hardness. Furthermore, it should be

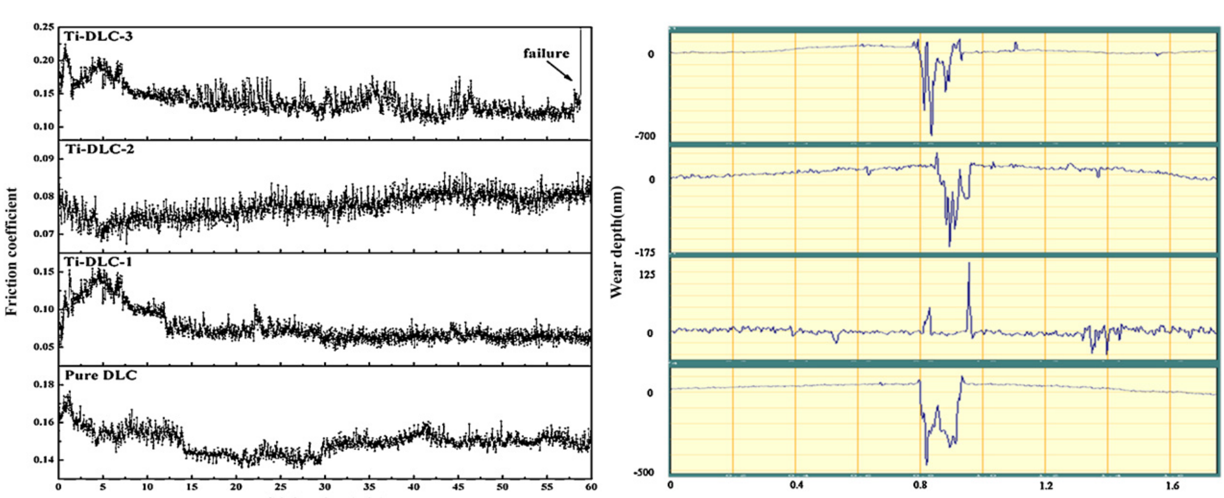

Fig. 7. (a) Friction coefficient of the films as a function of sliding distance and (b) corresponding surface profiles of the wear tracks after friction test.

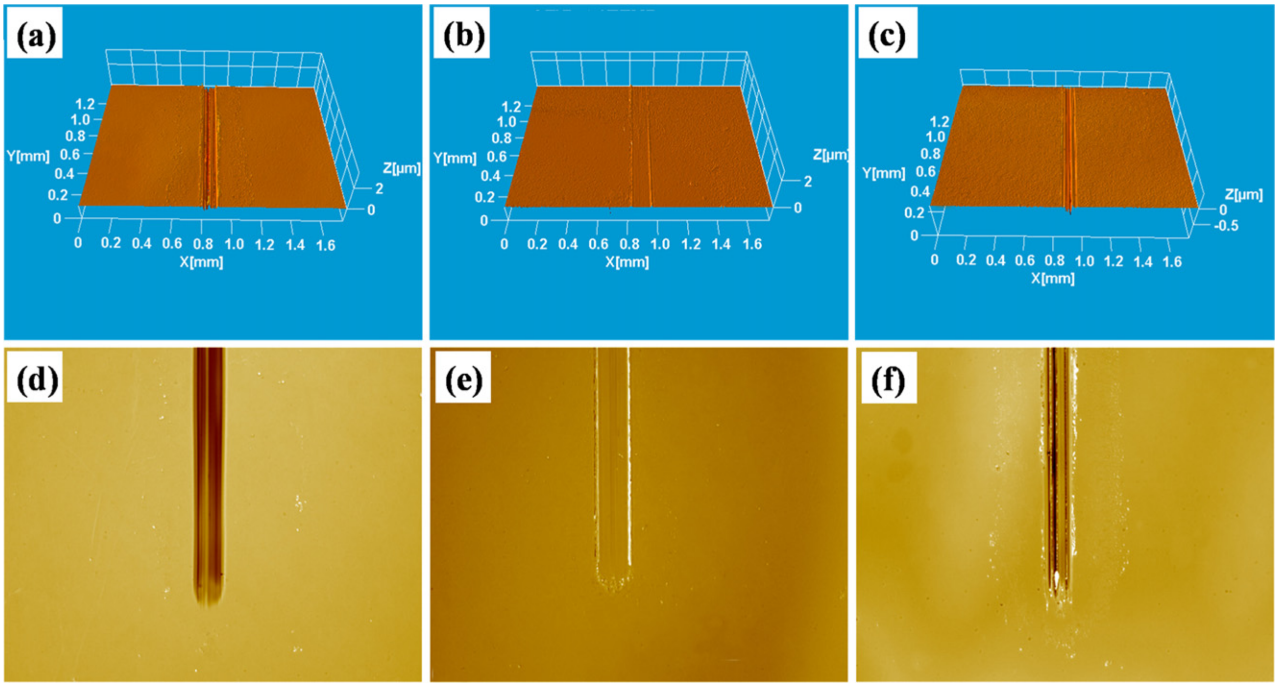

Fig. 9. The 3D images of the wear tracks of films deposited at the Ar/CH_4 flow ratios of (a and d) 0/250, (b and e) 60/190 and (c and f) 140/110.

noted that the hardness of the films with low Ti doping is retained at relatively high level (~13.75 GPa), although the stress is relaxed dramatically compared with the pure DLC films. That is, the films with low stress and high hardness could be obtained by low concentration Ti doping.

3.5. Tribological properties

Fig. 6 shows the comparison of friction behavior between ultralow Ti-doped DLC film and non-doped DLC film under the load of 10 N. Unlike the severely fluctuating friction coefficient with the sliding time for non-doped DLC film, the low Ti-doped DLC film shows a stable friction coefficient of about 0.05. Furthermore, it can also be found that when the sliding time reaches to 72 min, the non-doped DLC film fails with a higher friction coefficient (~0.157), while the low Ti-doped DLC film is still able to keep the stable friction behavior after 120 min without failure, which indicates low Ti doping considerably improves the excellent wear-resistance capacity of the DLC film compared to non-doped DLC films compared to non-doped DLC films, possibly due to the combinated protection of low stress and relatively high hardness.

Fig. 7 shows the friction coefficient of the films as a function of sliding distance and corresponding surface profiles of the wear tracks after friction test. Fig. 8 gives the average friction coefficient and wear rate of the films deposited at different Ar/CH_4 flow ratio. All Ti-doped DLC films show lower friction coefficient compared with the pure DLC film. Moreover, the Ti-DLC-3 and pure DLC film present deep and broad wear tracks, while the wear track of the Ti-DLC-1 film is smooth and indistinct. A protruding part of the two sides of the wear tracks for the Ti-DLC-1 film, around 50–150 nm higher above the film surface, could be observed, which may be due to the plastic deformation induced under high contact pressure [3]. The severely fluctuating friction coefficient curve could be observed for the pure DLC film. Meanwhile, the friction coefficient and wear rate are also kept at relatively high value of 0.157 and 9.57×10^{-9} mm^3/Nm, respectively. With the Ar/CH_4 flow ratio increases from 0/250 to 60/190, the friction coefficient of the film drops sharply to 0.05 and the wear rate reaches an extremely low value of 2.0×10^{-10} mm^3/Nm, almost 50 times lower than that of pure DLC film. As the Ar/CH_4 flow ratio increases further, the friction coefficient increases monotonically, which indicates low Ti doping could significantly improve the wear resistance performance of the DLC film. Moreover, it is noted that the Ti-DLC-3 film with 8.2% Ti doping fails after sliding for 58 min, the wear rate of 13.4×10^{-9} mm^3/Nm is extremely high, which implies the relatively high concentration Ti-doped DLC film possesses poor wear-resistance. The above mentioned well corresponding to the 3D images of wear tracks of the films deposited at Ar/CH_4 flow ratios of 0/250, 60/190 and 140/110 (Fig. 9), where the pure DLC film and Ti-DLC-3 film present more serious wear than Ti-DLC-1 film. At the same time, more debris are observed to pile up at the two sides and ends of the wear tracks, while less debris could be found at low Ti doping level. This excellent wear resistance performance may be attributed to the combination protection of low stress and high hardness.

4. Conclusions

Different concentration Ti-doped DLC films can be obtained using a magnetron sputtering Ti twin-target in the methane and argon mixture atmosphere by varying the Ar/CH_4 flow ratio. When the Ar/CH_4 flow ratio is 60/190, the doped Ti concentration in DLC film is so low (0.41%) that the TiC phase did not form, the film is of high hardness and low stress. However, when the Ar/CH_4 flow ratio increases further, the hardness decreased and the internal stress increased monotonically, which may be attributed to the formation of TiC phase. Moreover, the low concentration Ti-DLC film possesses excellent tribological properties, low wear rate of around 10^{-10} mm^3/Nm, almost 50 times lower than that of pure DLC film, and much lower friction coefficient of about 0.05. To dope Ti metal is a promising way to improve the mechanical and tribological properties of DLC films, however, to control the Ti metal concentration at very low level to make sure the doped Ti presenting in metallic status is the key factor. Very low Ti doping is confirmed to lower the internal stress while retaining the hardness, and to bestow the DLC film lower friction coefficient and excellent wear resistance.

Acknowledgments

The authors are grateful to the National Natural Science Foundation of China (grant no. 50823008, 50975273) and the Ministry of Science and Technology of China (grant no. 2010DFA63610) for financial support.

References

[1] D. Caschera, F. Federici, S. Kaciulis, Deposition of Ti-containing diamond-like carbon (DLC) films by PECVD technique [J], Materials Science and Engineering C 27 (2007) 1328–1330.
[2] W. Zhang, A. Tanaka, K. Wazumi, Y. Koga, Effect of environment on friction and wear properties of diamond-like carbon film, Thin Solid Films 413 (2002) 104.
[3] F. Zhao, H.-X. Li, L. Ji, Y.J. Wang, H.D. Zhou, J.M. Chen, Ti-DLC films with superior friction performance, Diamond & Related Materials 19 (2010) 342–349.
[4] W. Dai, H. Zheng, G. Wu, A. Wang, Effect of bias voltage on growth property of Cr-DLC film prepared by linear ion beam deposition technique, Vacuum 85 (2010) 231–235.
[5] R. Koppert, D. Goettel, O. Freitag-Weber, G. Schultes, Nickel containing diamond like carbon thin films, Solid State Sciences 11 (2009) 1797–1800.
[6] J. Veverkova, S.V. Hainsworth, Effect of temperature and counterface on the tribological Performance of W-DLC on a steel substrate, Wear 264 (2008) 518–525.
[7] G. Zhang, P. Yan, P. Wang, Y. Chen, J. Zhang, L. Wang, J. Zhang, The effect of applied substrate negative bias voltage on the structure and Properties of Al-containing a-C:H thin films, Surface & Coatings Technology 202 (2008) 2684–2689.
[8] J. Barriga, M. Kalin, K. Van Acker, K. Vercammen, A. Ortega, L. Leiaristi, Tribological performance of titanium doped and pure DLC coatings combined with a syntheticbio-lubricant, Wear 261 (2006) 9–14.
[9] J.-H. Ouyang, S. Sasaki, T. Murakami, Y. Zhou, J. Zhang, Mechanical and unlubricated tribological properties of titanium-containing diamond-like carbon coatings, Wear 266 (2009) 96–102.
[10] P.-C. Tsai, Y.-F. Hwang, J.-Y. Chiang, W.-J. Chen, The effects of deposition parameters on the structure and properties of titanium-containing DLC films synthesized by cathodic arc plasma evaporation, Surface & Coatings Technology 202 (2008) 5350–5355.
[11] V. Singh, J.C. Jiang, E.I. Meletis, Cr-diamond like carbon nanocomposite films: synthesis, characterization and properties, Thin Solid Films 489 (2005) 150–158.
[12] W. Dai, A. Wang, Deposition and properties of Al-containing diamond-like carbon films by a hybrid ion beam sources, Journal of Alloys and Compounds 509 (2011) 4626–4631.
[13] A.-Y. Wang, K.-R. Lee, J.-P. Ahn, J.H. Han, Structure and mechanical properties of W incorporated diamond-like carbon films prepared by a hybrid ion beam deposition technique, Carbon 44 (2006) 1826–1832.
[14] A.-Y. Wang, H.-S. Ahn, K.-R. Lee, J.-P. Ahn, Unusual stress behavior in W-incorporated hydrogenated amorphous carbon films, Applied Physics Letters 86 (2005) 111902.
[15] W. Dai, A. Wang, Synthesis, characterization and properties of the DLC films with low Cr concentration doping by a hybrid linear ion beam system, Surface & Coatings Technology 205 (2011) 2882–2886.
[16] W.J. Meng, B.A. Gillispie, Mechanical properties of Ti-containing and W-containing diamond-like carbon coatings, Journal of Applied Physics 84 (1998) 4314.
[17] B. Yang, Z.H. Huang, H.T. Gao, X.J. Fan, D.J. Fu, Droplet-free TiC nanocrystal-containing diamond-like carbon coatings deposited by combined cathodic arc MF magnetron sputtering, Surface & Coatings Technology 201 (2007) 6808–6811.
[18] P. Vijai Bharathy, D. Nataraj, P.K. Chu, H. Wang, Q. Yang, M.S.R.N. Kiran, J. Silvestre-Albero, D. Mangalaraj, Effect of titanium incorporation on the structural, mechanical and biocompatible properties of DLC thin films prepared by reactive-biased target ion beam deposition method, Applied Surface Science 257 (2010) 143–150.
[19] P. Wang, X. Wang, Y. Chen, G. Zhang, W. Liu, J. Zhang, The effect of applied negative bias voltage on the structure of Ti-doped a-C:H films deposited by FCVA, Applied Surface Science 253 (2007) 3722–3726.
[20] J. Robertson, Diamond-like amorphous carbon, Materials Science and Engineering: R: Reports 37 (2002) 129.