Graphite-like carbon films by high power impulse magnetron sputtering

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ABSTRACT

High-power impulse magnetron sputtering (HiPIMS), coupled with a direct-current magnetron sputtering (dcMS) in parallel, was employed to fabricate graphite-like amorphous carbon (GLC) films. Different impulse voltages were applied in HiPIMS during the film deposition. The structure and mechanical properties of the GLC films deposited by the HiPIMS were investigated. The bonding structure of the films was analyzed by X-ray photoelectron spectroscopy (XPS) and Raman spectroscopy. Atomic force microscopy (AFM) and Nano-indentation were used to characterize the surface quality and micro-hardness, respectively. Internal stress of the films was calculated based on the curvature measured by a laser tester. Tribological behavior of the GLC films is studied by a ball-on-disk tribometer in ambient condition. The effects of impulse voltage on deposition rate, internal stress, mechanical and tribological properties of the GLC films were investigated. The results are analyzed and discussed.

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1. Introduction

It is generally considered that hard carbon films must contain a high percentage of sp^3 bonds which have a structure of diamond, and the films with a high percentage of sp^2 bonds of carbon are soft because they are graphite-like [1]. This viewpoint needs to be modified since it has been revealed [2,3] that excellent mechanical properties including high hardness can also be achieved in sp^2-rich amorphous carbon films that have a dominant graphite-like structure. Graphite-like carbon (GLC) film is a kind of amorphous carbon and has prospective applications in surface modification due to their good chemical inertness, excellent friction and wear performance [4–6] as well as low internal stress, excellent conductivity and nice bio-compatibility [7]. Much attention has been attracted by GLC films, and many investigations on them have been carried out [8,9].

GLC films are usually fabricated by balanced/unbalanced magnetron sputtering and plasma-enhanced chemical vapor deposition techniques, where the low ionization of plasma results in less than desired mechanical and adhesive properties. It is necessary to find a new deposition technique to improve comprehensive properties of GLC films. High power impulse magnetron sputtering (HiPIMS) is

an ideal candidate. The HiPIMS exerts a pulsed and very high power onto the target, where plasma with electron density of $\sim 10^{19}$ m^{-3} is produced around the target surface. The ionization of HiPIMS is three orders of magnitude higher than that of conventional direct-current magnetron sputtering (dcMS) [10,11]. This high ionization is thought very effective to modify the structure and properties of films. It is reported that ultra-smooth, dense TiN and CrN films with good adhesion were realized using HiPIMS technique [12,13]. Recently, HiPIMS has been adopted to deposit amorphous carbon coatings [14–16].

Due to the discontinuity of sputtering, deposition rate of HiPIMS is low. This can be compensated by simultaneously employing a dcMS that supplies continuous sputtering. In this work, we superimpose HiPIMS onto dcMS to fabricate GLC films with enhanced properties. The microstructure, mechanical and tribological properties of the films are comparatively investigated when different impulse voltages are applied to HiPIMS that is in parallel with a constant direct current. The main factors influencing the tribological properties are discussed in terms of hybrid state of carbon atoms.

2. Experimental details

The sputtering system for film deposition is characterized by the HiPIMS power supply that is superimposed to a dcMS one. The HiPIMS and the dcMS supply sputtering power in parallel to the carbon target (380 mm × 140 mm × 7 mm). The HiPIMS power supply was produced by the State Key Laboratory of Advanced Welding

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Table 1
Deposition conditions for GLC films.

Sample	Direct-current (A)	Impulse voltage (V)	Ar flow (sccm)	Bias voltage (V)
dcMS	1.0	–	50	200
HiPIMS 750 V	1.0	750	50	200
HiPIMS 900 V	1.0	900	50	200
HiPIMS 1000 V	1.0	1000	50	200

Production and Technology, Harbin Institute of Technology, China. In this work, GLC films were deposited at different impulse voltages for HiPIMS, keeping the dcMS with a constant current of 1.0 A. The impulse frequency is 50 Hz and the impulse width was 65 μs. In case the HiPIMS was closed, the films were fabricated simply by dcMS. The effects of HiPIMS and its impulse voltage on the structure and properties of DLC films are investigated comparatively with dcMS. The detailed deposition parameters are listed in Table 1.

The GLC films were deposited onto carefully polished M2 high-speed steel and thick/thin Si wafer substrates that are about 150 mm away from the target. The high-speed steel was used for tribological testing, the thick Si wafers (20 mm × 15 mm × 0.7 mm) for observations of film microstructures and the thin Si wafers (20 mm × 15 mm × 0.285 mm) for estimation of internal stress. All the substrates were cleaned ultrasonically in ethanol and acetone baths for 20 min and then dried before being put into the deposition chamber. Once the background vacuum lower than 3×10^{-5} Torr was achieved, argon with purity higher than 99.99% was introduced. The substrates were immersed in Ar plasma glow at a bias voltage of 500 V for 20 min so as to remove the oxide layer or impurities on the substrate surface before deposition. A graphite target that has purity better than 99.99% was employed as a carbon source for GLC films. The work pressure was kept at 2.1 mTorr and no heater was used during the deposition. The GLC films were deposited directly onto the substrates without an underlayer.

Film thickness was measured by a profiler and the deposition rate was obtained based on the deposition time. The Axis ultra-DLD X-ray photoelectron spectroscopy (XPS) operating with Al Kα irradiation at energy of 160 eV was employed to characterize the chemical bonding of the films. The RENISHAW Raman spectroscopy using 633 nm line of Ar⁺ laser was adopted to investigate bonding structure of the films. Typical acquisition time was 10 s and the spectra were recorded in range of 1000–2000 cm⁻¹ for reliable fitting. Gaussian is applied in the peak-split of the Raman spectrum. Surface morphology and roughness of the films were observed by atomic force microscopy (AFM). The MTS nano-indenter was adopted to measure hardness and elastic modulus. Curvature of the film/substrate was determined by a laser tester and internal stress was calculated using the Stoney equation. Tribological behavior of the GLC films were investigated under dry-sliding conditions at room temperature in air by the ball-on-disk tribo-meter. The load of 3 N was kept for 2000 s at a sliding speed of 100 mm/s, and the radius was 3 mm. The wear traces were observed by scanning electron microscopy (SEM).

3. Results and discussion

3.1. Deposition rate

The deposition rate of GLC films at different deposition conditions is illustrated in Fig. 1, from which one can see that the deposition rate of the GLC film deposited by dcMS is 2.0 nm/min. It is well known that deposition rate of the films strongly depends on sputtering rate of the target. When the HiPIMS is superimposed, both ionization ratio and sputtering rate are elevated, and thus the deposition rate is enhanced. The deposition rate of HiPIMS
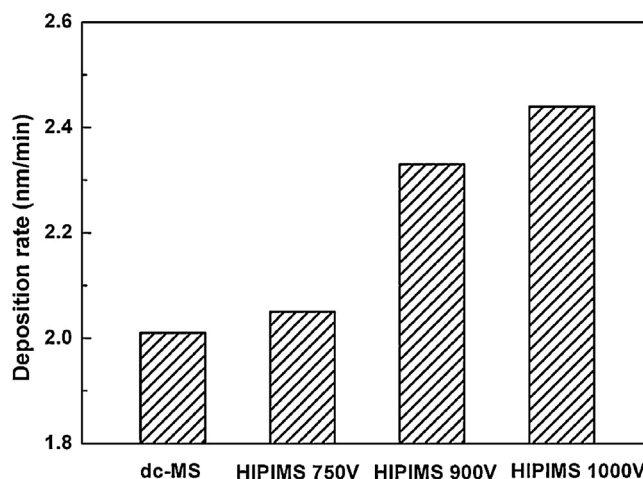

Fig. 1. Deposition rate of the GLC films.

increases with increasing impulse voltage. The higher the impulse voltage, the faster the deposition rate is. The maximum rate of 2.43 nm/min is obtained at 1000 V impulse voltage, where the highest sputtering power is achieved. One may imagine that more neutral radicals and ionic radicals are sputtered from the target surface at higher impulse voltages, where higher ionization ratio is realized.

3.2. Microstructural and chemical characterization

XPS spectroscopy is a powerful tool to determine chemical bonds of materials since each element has a unique set of binding energies. C1s peaks in the XPS spectrum are usually used to identify chemical states of the amorphous carbon films. The XPS C1s spectra of the GLC films are shown in Fig. 2, where there exists an obvious peak of carbon. The peak can be split into three peaks, i.e. the C=C peak at 284.4 eV (sp^2 bond), the C—C peak at 285.8 eV (sp^3 bond) and the C—O peak at 286.7 eV [17,18,19], as indicated in Fig. 2. The weak C—O peak implies that the surface of the GLC films was slightly oxidized since the measurement was executed after the samples were lift out from the chamber and exposed to the atmosphere. According to the split peaks, estimated sp^2/sp^3 ratio is 67/33, 62/38, 66/34 while an impulse voltage of 750 V, 900 V, and 1000 V is applied to the HiPIMS, respectively. And the ratio for the dcMS is about 60/40. See Table 2. It is seen that all the films are
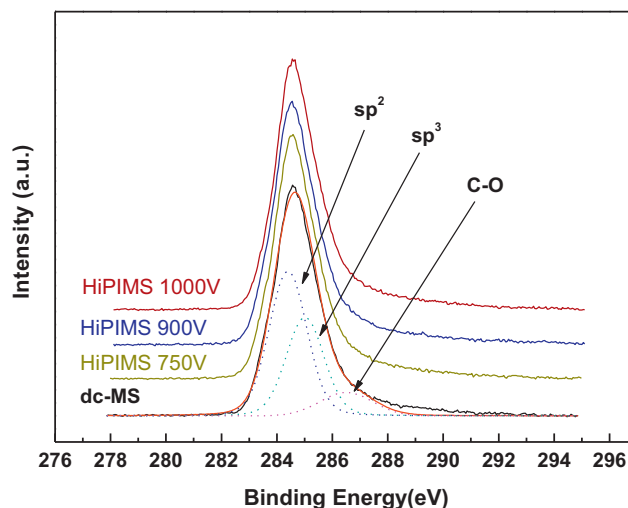

Fig. 2. XPS C1s spectra of the GLC films deposited at different conditions.

Table 2
Some data derived from Raman and XPS spectra of the GLC films.

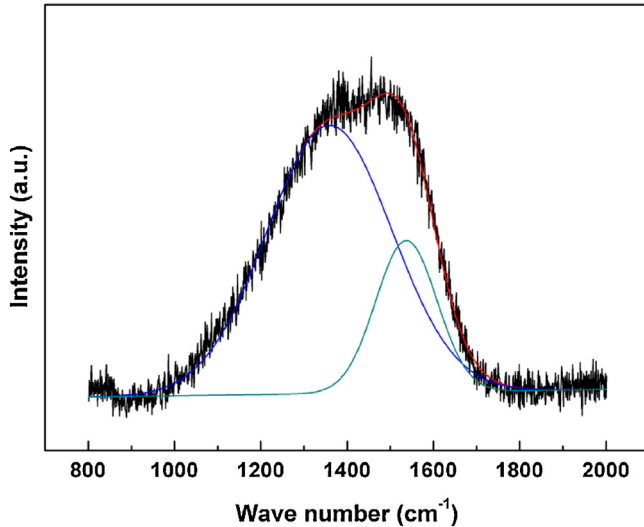| Sample	A_D/A_G	Pos(D)	Pos(G)	FWHM(G)	sp^2/sp^3 ratio
dcMS	3.81	1358.77	1536.64	168.49	60/40
HiPIMS 750 V	4.50	1360.14	1538.58	165.765	67/33
HiPIMS 900 V	4.43	1358.45	1538.06	171.738	62/38
HiPIMS 1000 V	4.70	1362.25	1540.79	164.434	66/34

Fig. 3. Typical Raman spectrum of the GLC films deposited at different conditions. Only the curve of the film fabricated by HiPIMS with impulse voltage of 750 V is shown here.

dominated by sp^2 sites, revealing that the deposited layers are GLC films. This is confirmed by the results of Raman spectrum displayed in Fig. 3, which is from the sample of HiPIMS 750 V and is a typical spectrum of GLC films.

Raman spectroscopy is one of the most popular and powerful tools used to probe the quality of carbon-based materials because it is sensitive to π bonds [20]. Raman spectra of the amorphous carbon films are characterized by a D peak around 1360 cm^{-1} and a G peak around 1560 cm^{-1} in the wave number range of 800–2000 cm^{-1}, corresponding to visible excitation. The D peak is due to the breathing modes of sp^2 atoms in rings and the G peak is due to the bond stretching of all pairs of sp^2 atoms in both rings and chains [21,22]. One can see from Fig. 3 that they have an intensive D band and a weak shoulder G band in the Raman spectrum, which confirms that the deposited layers are mainly consisted of GLC films. More detailed information extracted from the Raman spectrum is shown in Table 2, where the value of A_D/A_G is a measure of the size of the sp^2 phase organized in rings while both the G peak position (Pos(G)) and the full width at half maximum (FWHM(G)) indicate disorder of the films. A_D/A_G is the area ratio of the split two peaks. The Pos(G) is sensitive to topological disorder arising from the size and shape distribution of sp^2 clusters while the FWHM(G) sensitive to structural disorder arising from bond angle and bond length distortions [22,23]. Large A_D/A_G, high Pos(G) and low FWHM(G) imply the sp^2 content is high while the sp^3 content is low in the amorphous carbon [4,23,24]. According to Table 2, the GLC films deposited by HiPIMS have higher content of sp^2 than those by dcMS. Moreover, in the GLC films deposited by HiPIMS, the fraction of sp^2 bonds decreases when the impulse voltage increases from 750 V to 900 V, but it then increases as the impulse voltage is further increased to 1000 V. These results are consistent well with those obtained by previous XPS analysis.

The fraction of sp^2 bonds in the GLC films depends on the deposition temperature and ion energy, which increases with increasing impulse voltage [25]. At an impulse voltage of 750 V, average energy of the carbon ions or particles is not high enough and they form a film with graphite-like bonds. As the impulse voltage is increased to 900 V, both the ionization ratio and the average energy of the carbon ions are enhanced, giving rise to the combination of carbon atoms with sp^3 bonds. However, while the impulse voltage is further increased to 1000 V, strong bombardment of ions during the deposition brings excessive heat, which makes the sp^3 sites transit to sp^2 sites [1,26]. The enhanced temperature at the surface of the film is advantageous for the formation of sp^2 clusters as well [27].

Surface quality of the GLC films was examined by AFM. The morphology and corresponding roughness are shown in Fig. 4. It can be
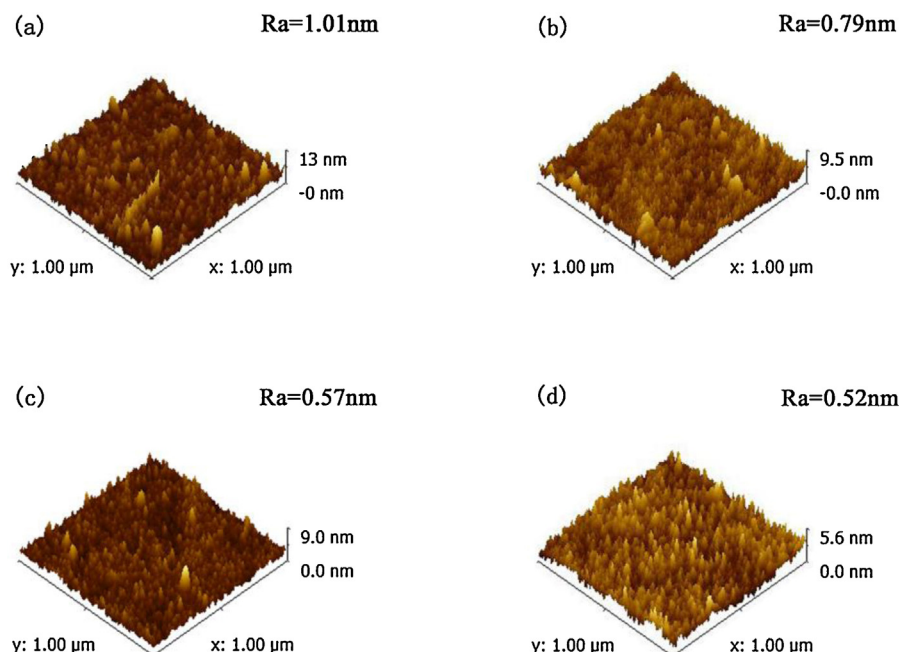

Fig. 4. Morphology and roughness observed by AFM for the GLC films deposited by dcMS (a), HiPIMS 750 V (b), HiPIMS 900 V (c), and HiPIMS 1000 V (d), respectively.

Fig. 5. Hardness and elastic modulus of the GLC films deposited at different conditions.

seen that all the films are flat, smooth and compact. The GLC film deposited by dcMS has the largest roughness 1.01 nm, while those by HiPIMS have better surface quality. The roughness monotonically decreases with increasing impulse voltage, from 0.79 nm at 750 V to 0.52 nm at 1000 V. The ion energy during deposition plays an important role in surface morphology of the GLC films. In case of dcMS, the ionization is low and the carbon ions deposit with low energy, and thus loose film with a relative large roughness [8] is formed. When HiPIMS is superimposed to dcMS, both plasma density and ion energy are increased. As a result, the energy input during the deposition is increased and the deposition temperature is elevated, which is favorable for the deposited atoms to move or diffuse leading to a reduced surface roughness [28,29]. The larger the impulse voltage, the higher the temperature, and thus the lower the roughness. It is also considered that the etching effects caused by the ion bombardment under high impulse voltages may reduce the surface roughness [29,30].

3.3. Mechanical properties of GLC films

Fig. 5 gives hardness and elastic modulus of the GLC films deposited at different conditions. It can be seen that both hardness and elastic modulus of the GLC films deposited by HiPIMS, when compared to those by dcMS, are slightly increased at an impulse voltage of 750 V. The values further increase while the voltage is increased to 900 V, but they decrease while a voltage of 1000 V is applied.

Both hardness and elastic modulus are comprehensive performance of films, since they are affected by several factors. It has been reported that hardness of amorphous carbon films are strongly dependent on sp^3 bonds [18,31]. Internal stress also contributes to hardness as well as elastic modulus of the films [18]. Fig. 6 gives the internal stress of the GLC films deposited by both dcMS and HiPIMS. One can see the internal stress of the film fabricated by dcMS is the lowest. As HiPIMS is applied, with increasing impulse voltages, internal stress increases monotonously, which is corresponding to the strong ion bombardment during the deposition. According to the hardness results shown in Fig. 5, the maximum hardness of 12.2 GPa and modulus of 187.7 GPa are achieved at an impulse voltage of 900 V. Whereas hardness of the film deposited at the voltage of 1000 V, where there exist the largest internal stress, is even lower than that of the film deposited by dcMS. This implies that the content of sp^3 sites, as indicated in Table 2, is the most important factor affecting hardness of the GLC film.

Regardless of its variation with the impulse voltage, hardness values of the GLC coatings in this work (10.04–12.17 GPa) are comparable to or even higher than those (7.2–11.7 Gpa) obtained by
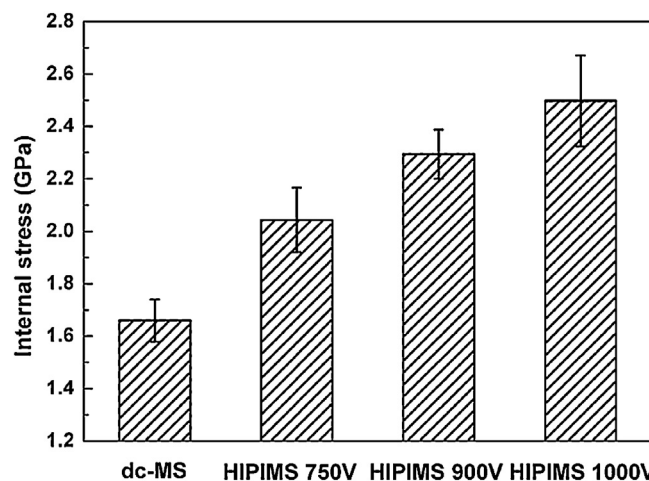
unbalanced magnetron sputtering [32]. One can see that the HiPIMS is favorable to the hardness of the GLC films.

3.4. Tribological properties of GLC films

Fig. 7 presents the friction curves of the GLC films deposited by dcMS and HiPIMS with different impulse voltages. The friction coefficient of the films deposited by dcMS increases suddenly and becomes unsteady after being ground about 120 m in the test. The tribological behavior of the GLC films deposited by HiPIMS is improved since the friction coefficients keep constant during the whole testing process, exhibiting steady friction properties. It should be noted that the highest value of friction coefficients is obtained for the film fabricated at 900 V, where the hardness is maximum (Fig. 5) and roughness is relatively low (Fig. 4(c)). This can be explained by the XPS results of sp^2/sp^3 ratio illustrated in Table 2. The smallest sp^2/sp^3 ratio is found at the impulse voltage of 900 V. It is indicated that content of sp^2 is the main factor that contributes to the tribological properties of the GLC films [31]. The GLC films containing higher content of sp^2 exhibit usually lower friction coefficients since there are less dangling σ bonds and thus lower surface energy [8]. The sp^2 clusters within the GLC films also serve as solid lubricant during the tribological test, which also helps to reduce the friction coefficients [19,29].

The wear traces of the tribological test were observed by SEM, as displayed in Fig. 8. It can be seen clearly that the worn trace
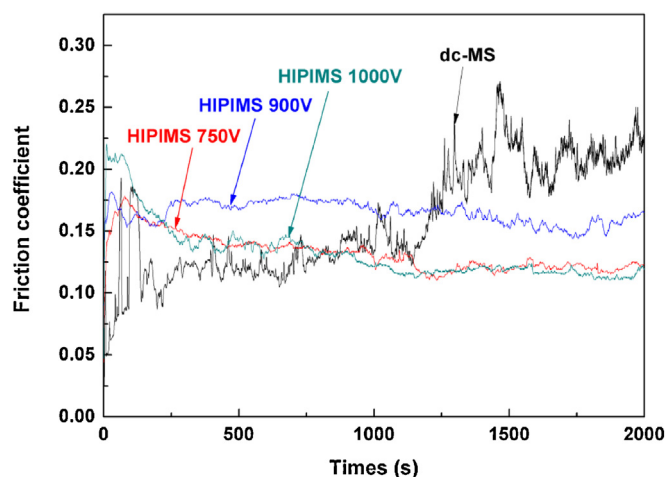

Fig. 6. Internal stress of the GLC films deposited at different conditions.

Fig. 7. Friction curves of the GLC films deposited at different conditions.
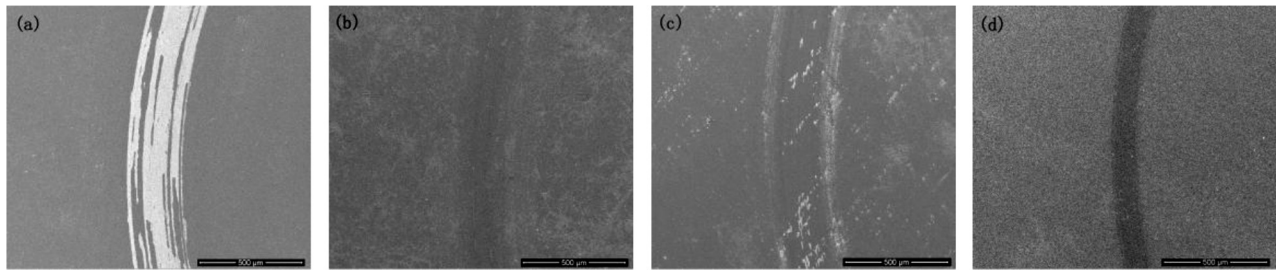
Fig. 8. SEM images of wear traces of the GLC films deposited at different conditions: (a) dcMS, (b) HiPIMS 750 V, (c) HiPIMS 900 V, (d) HiPIMS 1000 V, respectively.

of the GLC film deposited by dcMS (Fig. 8(a)) is more significant than those (Fig. 8(b)–(d)) by HiPIMS. The obvious delamination of the coating in Fig. 8(a) is responsible for the sudden increase of friction coefficient when the dcMS coating is ground about 120 m (see Fig. 7). The film deposited with an impulse voltage of 900 V has a relative deep and wide worn trace when compared with those deposited at 700 V or 1000 V. These results confirm that the sp^2 content in the GLC film is a key factor affecting the tribological behavior, which means that the films containing less sp^2 content are worn more significantly.

4. Conclusions

GLC films were prepared by HiPIMS as well as dcMS. The results show that microstructure, mechanical and tribological properties of the GLC films are strongly dependent on the impulse voltage of the HiPIMS that is coupled with a dcMS. It is easier to get sp^2 bond-rich GLC films by using HiPIMS technique. While roughness decreases monotonously as the impulse voltage increases and the highest hardness is obtained at 900 V, steady wear behavior and low friction coefficients are achieved at 750 V and 1000 V instead. It is thought that sp^2 bonds are responsible for the lubrication while sp^3 bonds contribute to the hardness, since the minimum fraction of sp^2 bonds (or the maximum fraction of sp^3 bonds) is obtained by HiPIMS at 900 V.

Acknowledgements

References

[1] J. Robertson, Diamond-like amorphous carbon, Mater. Sci. Eng. Rep. 37 (2002) 129.

[2] T. Zaharia, P. Kudlacek, M. Creatore, R. Groenen, P. Persoone, M.C.M. van de Sanden, Improved adhesion and tribological properties of fast-deposited hard graphite-like hydrogenated amorphous carbon films, Diamond and Related Materials 20 (2011) 1266.

[3] G.A.J. Amaratunga, M. Chhowalla, C.J. Kiely, I. Alexandrou, R. Aharonov, R.M. Devenish, Hard elastic carbon thin films from linking of carbon nanoparticles, Nature 383 (1996) 321.

[4] Y.S. Park, H.S. Myung, J.G. Han, B. Hong, The electrical and structural properties of the hydrogenated amorphous carbon films grown by close field unbalanced magnetron sputtering, Thin Solid Films 482 (2005) 275.

[5] H.X. Li, T. Xu, J.M. Chen, H.D. Zhou, H.W. Liu, The effect of applied dc bias voltage on the properties of aC: H films prepared in a dual dc–rf plasma system, Applied Surface Science 227 (2004) 364.

[6] M. Rybachuk, J.M. Bell, The effect of sp^2 fraction and bonding disorder on micro-mechanical and electronic properties of aC: H films, Thin Solid Films 515 (2007) 7855.

[7] R. Olivares, S.E. Rodil, H. Arzate, Osteoinduction properties of graphite-like amorphous carbon films evaluated in-vitro. Osteoinduction properties of graphite-like amorphous carbon films evaluated *in-vitro*, Diamond and Related Materials 16 (2007) 1858.

[8] Y. Wang, L. Wang, Q. Xue, Improving the tribological performances of graphite-like carbon films on Si_3N_4 and SiC by using Si interlayers, Applied Surface Science 257 (2011) 10246.

[9] Y. Wang, L. Wang, G. Zhang, S.C. Wang, R.J.K. Wood, Q. Xue, Effect of bias voltage on microstructure and properties of Ti-doped graphite-like carbon films synthesized by magnetron sputtering, Surface and Coatings Technology 205 (2010) 793.

[10] V. Kouznetsov, K. Macák, J.M. Schneider, U. Helmersson, I. Petrov, A novel pulsed magnetron sputter technique utilizing very high target power densities, Surface and Coatings Technology 122 (1999) 290.

[11] J. Alami, J.T. Gudmundsson, J. Bohlmark, J. Birch, U. Helmersson, Plasma dynamics in a highly ionized pulsed magnetron discharge, Plasma Sources Science and Technology 14 (2005) 525.

[12] K. Macak, V. Kouznetsov, J. Schneider, U. Helmersson, I. Petrov, Ionized sputter deposition using an extremely high plasma density pulsed magnetron discharge, Journal of Vacuum Science and Technology A 18 (2000) 1533.

[13] A. Anders, J. Andersson, A. Ehiasarian, High power impulse magnetron sputtering: current–voltage–time characteristics indicate the onset of sustained self-sputtering, Journal of Applied Physics 102 (2007) 113303.

[14] K. Sarakinos, A. Braun, C. Zilkens, S. Mráz, J.M. Schneider, H. Zoubos, P. Patsalas, Exploring the potential of high power impulse magnetron sputtering for growth of diamond-like carbon films, Surface and Coatings Technology 206 (2012) 2706.

[15] A. Aijaz, D. Lundin, N. Brenning, U. Helmersson, A strategy for increase carbon ionization in magnetron sputtering discharges, Diamond and Related Materials 23 (2012) 1.

[16] S. Schmidt, Zs. Czigány, G. Greczynski, J. Jensen, L. Hultman, Ion mass spectrometry investigations of the discharge during reactive high power pulsed and direct current magnetron sputtering of carbon in Ar and Ar/N2, Journal of Applied Physics 112 (2012) 013305.

[17] P.K. Chu, L. Li, Mater characterization of amorphous and nanocrystalline carbon films, Chemical Physics 96 (2006) 253.

[18] Y. Wang, H. Li, L. Ji, F. Zhao, Q. Kong, Y. Wang, X. Liu, W. Quan, H. Zhou, J. Chen, Microstructure, mechanical and tribological properties of graphite-like amorphous carbon films prepared by unbalanced magnetron sputtering, Surface and Coatings Technology 205 (2011) 3058.

[19] X. Wang, P. Wang, S. Yang, J. Zhang, Tribological behaviors of fullerene-like hydrogenated carbon (FL-C: H) film in different atmospheres sliding against Si_3N_4 ball, Wear 265 (2008) 1708.

[20] S.E. Rodil, A.C. Ferrari, J. Robertson, W.I. Milne, Raman and infrared modes of hydrogenated amorphous carbon nitride, Journal of Applied Physics 89 (2001) 5425.

[21] A.C. Ferrari, J. Robertson, Resonant Raman spectroscopy of disordered, amorphous, and diamondlike carbon, Physical Review B 64 (2001) 075414.

[22] C. Casiraghi, A. Ferrari, J. Robertson, Raman spectroscopy of hydrogenated amorphous carbons, Physical Review B 72 (2005) 085401.

[23] A. Ferrari, J. Robertson, Interpretation of Raman spectra of disordered and amorphous carbon, Physical Review B 61 (2000) 14095.

[24] J. Filik, P.W. May, S.R.J. Pearce, R.K. Wild, K.R. Hallam, X.P.S. laser, Raman analysis of hydrogenated amorphous carbon films, Diamond and Related Materials 12 (2003) 974.

[25] D. Horwat, A. Anders, Compression and strong rarefaction in high power impulse magnetron sputtering discharges, Journal of Applied Physics 108 (2010) 123306.

[26] E. Liu, L. Li, B. Blanpain, J.P. Celis, Residual stresses of diamond and diamondlike carbon films, Journal of Applied Physics 98 (2005) 073515.

[27] 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 aC: H films deposited by FCVA, Applied Surface Science 253 (2007) 3722.

[28] Y. Wang, H. Li, L. Ji, F. Zhao, X. Liu, Q. Kong, Y. Wang, W. Quan, H. Zhou, J. Chen, The effect of duty cycle on the microstructure and properties of graphite-like amorphous carbon films prepared by unbalanced magnetron sputtering, Journal of Physics D: Applied Physics 43 (2010) 505401.

[29] Y. Lifshitz, R. Edrei, A. Hoffman, E. Grossman, G.D. Lempert, J. Berthold, B. Schultrich, H.U. Jäger, Surface roughness evolution and growth mechanism of carbon films from hyperthermal species, Diamond and Related Materials 16 (2007) 1771.

[30] C. Casiraghi, A. Ferrari, R. Ohr, A. Flewitt, D. Chu, J. Robertson, Dynamic roughening of tetrahedral amorphous carbon, Physical Review Letters 91 (2003) 226104.

[31] Y. Wang, Y. Ye, H. Li, L. Ji, J. Chen, H. Zhou, A magnetron sputtering technique to prepare aC: H films: effect of substrate bias, Applied Surface Science 257 (2011) 1990.

[32] J. Chen, Y. Wang, H. Li, L. Ji, Y. Wu, Y. Lv, X. Liu, Y. Fu, H. Zhou, Microstructure, morphology and properties of titanium containing graphite-like carbon films deposited by unbalanced magnetron sputtering, Tribology Letters 49 (2013) 47.