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Studies of diamond-like carbon (DLC) films deposited on stainless steel substrate with Si/SiC intermediate layers

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In this work, diamond-like carbon (DLC) films were deposited on stainless steel substrates with Si/SiC intermediate layers by combining plasma enhanced sputtering physical vapour deposition (PEUMS-PVD) and microwave electron cyclotron resonance plasma enhanced chemical vapour deposition (MW-ECRPECVD) techniques. The influence of substrate negative self-bias voltage and Si target power on the structure and nano-mechanical behaviour of the DLC films were investigated by Raman spectroscopy, nano-indentation, and the film structural morphology by atomic force microscopy (AFM). With the increase of deposition bias voltage, the G band shifted to higher wave-number and the integrated intensity ratio I_D/I_G increased. We considered these as evidences for the development of graphitization in the films. As the substrate negative self-bias voltage increased, particle bombardment function was enhanced and the sp^3-bond carbon density reducing, resulted in the peak values of hardness (H) and elastic modulus (E). Silicon addition promoted the formation of sp^3 bonding and reduced the hardness. The incorporated Si atoms substituted sp^2- bond carbon atoms in ring structures, which promoted the formation of sp^3-bond. The structural transition from C–C to C–Si bonds resulted in relaxation of the residual stress which led to the decrease of internal stress and hardness. The results of AFM indicated that the films was dense and homogeneous, the roughness of the films was decreased due to the increase of substrate negative self-bias voltage and the Si target power.

Keywords: diamond-like carbon (DLC), stainless steel substrate, intermediate layers
PACC: 8115H, 3320F, 0779

1. Introduction

Diamond-like carbon (DLC) films have been studied extensively and utilized industrially for their superior properties such as hardness, low friction coefficient and high wear resistance, high electrical resistance, low dielectric constant, chemical inertness to acid and alkalis, optical transparency, etc.[1] There is also a growing market for the use of DLC in wear-resistant applications, for example on cutting tools, automotive components and orthopaedic prostheses. However, a number of problems have been encountered in their use. DLC in the form of hydrogenated amorphous carbon (a-C:H) presents limited thermal stability, poor adhesion to some substrates including stainless steels and high residual stress.[2] Many investigations have been dedicated to the introduction of additional elements, such as fluorine, nitrogen, silicon and various metals in the carbonaceous structure to improve the properties of conventional DLC coatings.[3−7]

In particular, the incorporation of Si into DLC films stabilizes the sp^3 bonding, reduces the stress, makes the friction coefficient independent of the humidity, improves adhesion to metal substrates, and increases the thermal stability.[8−11] However, its influence on the nanomechanical properties is rather controversial and is generally not directly related to the sp^3 bonding in the films. Hardness and elastic modulus have been reported to either increase or decrease or even remain constant upon initial incorporation of silicon.[12−14] It is obvious that the effect of Si on the nanomechanical behaviour of DLC films is not well understood and requires further investigation.

In this paper, diamond like carbon films were deposited successfully through preparation of Si/SiC intermediate layers on stainless steels surface by combin-

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ing MW-ECR PECVD and PEUMS-PVD techniques. This technique embodies an effort to use silicon target and methane (CH_4) to produce Si/SiC intermediate layers, graded in carbon composition, to improve the adherence of DLC films to the metal. The requirements for effective protection include chemical inertness together with microstructural demands, such as high hardness and high elastic modulus, smooth surface, homogeneous stoichiometry, stress-free layers and good adhesion between the coating and the substrate material. The investigation indicates that the characteristics of DLC films are dependent on both the substrate negative self-bias voltage and the silicon target power applied during the film deposition process. In this study, the microstructure and nanomechanical characteristics of the films were investigated by Raman spectroscopy, nanoindentation and AFM.

2. Experimental

The depositions of DLC films were performed using the plasma source ion implantation (PSII) system. The substrate holder was grounded and placed 15 cm away from the sputtering target. The feed gases, CH_4 and Ar were introduced into the system whereas the gas flow was measured by mass flow controllers, and the pressure was monitored by a vacuum gauge. The base pressure in the deposition chamber was 3.0×10^{-3} Pa and films were deposited at a microwave power of 850 W (radio frequency 2.45 GHz), and at a constant total pressure of 2.0×10^{-1} Pa. Since the substrate was not intentionally heated, its temperature depended to some degree on the plasma power.

The stainless steel substrates (304 stainless steel, $10\times10\,mm^2$) were metallographically polished to obtain mirror-like surface, cleaned in ultrasonic baths of acetone and methanol and then dried with a nitrogen flow. Prior to deposition, the substrates were plasma cleaned using argon at a flow rate of 30sccm, self-bias of –300 V for 10 minutes to avoid any contamination. Si/SiC intermediate layers were deposited on stainless substrates with Si target and CH_4 as precursors by combining PEUMS-PVD and MW-ECRPECVD techniques. The Si content of the films was controlled by changing the input RF power applied to the silicon target. And then the DLC films were deposited on Si/SiC intermediate layers continuously by MW-ECRPECVD. The experimental conditions are given in Table 1.

Raman spectroscopy (RENISHAW INVIA) with excitation by an Ar ion laser at 632.8 nm was used, with a spectral resolution of $2\,cm^{-1}$. To minimize heating damage during measurement, the laser output power was fixed at 35 mW. Hardness (H) and elastic modulus (E) of the films were measured by MTS Nanoindenter XP. An indentation load of 500 mN was used in this work, where the maximum penetration depth was less than 500 nm. The structural morphology of the films was analysed by AFM (Nanoscope III Scanning Probe Microscope), from which the root mean square (RMS) roughness could be determined.

Table 1. Deposition conditions for the diamond-like carbon films synthesis.

A. Si intermediate layers	
Si target power/W	100–300
Ar flow rate/sccm	20
Substrate negative self-bias voltage/V	100
Sputtering time/min	30
B. SiC intermediate layers	
Si target power/W	100–300
Deposition gases	
Ar/sccm	10
CH_4/sccm	40
Substrate negative self-bias voltage/V	100
Deposition time/min	30
C. DLC film	
Deposition gases	
Ar/sccm	10
CH_4/sccm	40
Substrate negative self-bias voltage/V	100–300
Deposition time/min	30

3. Results and discussion

3.1. Raman spectra analysis

Raman spectra of DLC films deposited under different substrate negative self-bias voltages are shown in Fig.1. The Raman spectrum of DLC films consists of a main band at 1580 cm^{-1} due to the lattice vibration of sp^2 carbon atoms (G peak), and a low frequency modulation corresponding to the disorder-allowed zone edge mode of graphite (D peak) at 1360 cm^{-1}. The spectra are characteristic of typical DLC structure.[15−17] All spectra are fitted with a combination of two Gaussian curves for the G peak and D peak. Raman spectroscopy investigation includes the band position for the D and G peaks, the I_D/I_G ratios and the full-width at half-maximum (FWHM) for both peaks, as shown in Table 2.

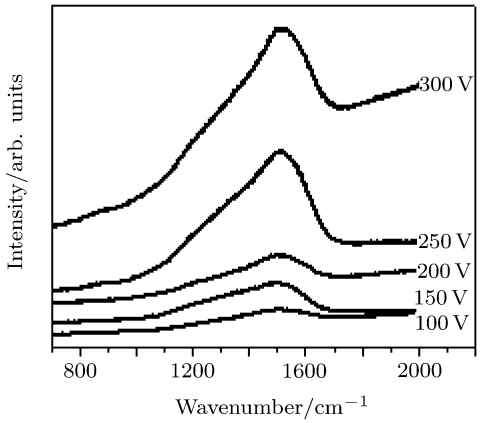


Fig.1. Raman spectra for a series of DLC films with different substrate negative self-bias voltages.

Table 2. Fitted Raman parameters for a series of DLC films with different substrate negative self-bias voltages.

Substrate negative self-bias voltage/V	Band position/cm^{-1}		FWHM/cm^{-1}		Intensity ratio
	D	G	D	G	I_D/I_G
100	1307.31	1515.72	268.04	214.55	0.59
150	1337.75	1527.15	315.18	195.36	0.61
200	1340.08	1530.50	252.04	204.90	0.89
250	1354.92	1535.41	317.37	185.37	1.36
300	1356.91	1544.52	275.56	182.84	1.39

It can be seen that the I_D/I_G ratio appears to increase with increasing substrate negative self-bias voltage. The position of the D peak increased from ∼1307.31 cm^{-1} at 100 V bias to 1356.91 cm^{-1} at 300 V bias. A peak which we associate with the G peak appeared to shift from 1515.72 to 1544.52 cm^{-1}. The shift of G peak position towards higher wave numbers and the increase of I_D/I_G ratio with the increase of substrate negative self-bias voltage resulted from the structural change towards graphite-like structure. It has been reported that the FWHM of G peak may be related to the graphitic cluster size and internal stress of carbon film, the G peak position may be associated with the hydrogen content in amorphous films. The higher G band position in the Raman spectrum and lower background slope indicate lower hydrogen content in the DLC films.[18,19] The FWHM of G peak appears to decrease with increasing substrate negative self-bias voltage, namely, the size of graphite crystallites decreases with increasing substrate negative self-bias voltage. These trends imply that graphite crystallites become finer when ions with higher energy bombard the surface of growing film, or a film is deposited under a higher degree of gas decomposition. The increase in substrate temperature induced by higher energetic ion bombardment promoted the film graphitization too.

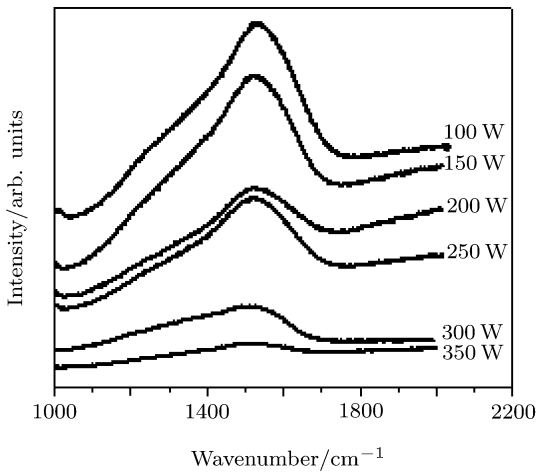


Fig.2. Raman spectra for a series of DLC films with different Si target power.

Figure 2 shows a series of Raman spectra of the DLC films with different Si target power. It is clear that the Raman line shape changes from asymmetric

to more symmetric with silicon incorporation. The fitting results for the spectra are given in Table 3.

Evidently, both D and G peak positions shift to lower Raman frequency with increasing Si. In addition, the I_D/I_G ratio decreases and the D peak ultimately disappears when the Si target power reaches 350 W. Various reasons can account for the trends observed. The shift of the G peak position to lower frequency can be partially attributed to a reduction in compressive stress when silicon is introduced into the films, because the longer de-strained bonds vibrate at lower frequency.[10] The presence of Si–C bridging bonds can also weaken the adjacent C–C bonds, resulting in a downward frequency shift of the D and G peaks and a decrease in the I_D/I_G ratio. On the other hand, the simultaneous downshift and decrease in I_D/I_G ratio can also be accounted for by the creation of higher disorder in the film.[20] The latter suggests that Si doping reduces the average size of the sp^2-bonded carbon and promotes the formation of sp^3-bonding in the DLC films. The enhancement of sp^3-bonding is related to the Si valence structure, which is well known to form only four-fold coordinated networks (Si–C).

Table 3. Fitted Raman parameters for a series of DLC films with different Si target power.

Si target power/W	Band position/cm^{-1}		FWHM/cm^{-1}		Intensity ratio
	D	G	D	G	I_D/I_G
100	1356.91	1544.51	304.19	224.44	1.03
150	1338.60	1532.52	296.14	212.64	0.90
200	1340.08	1530.50	252.04	214.90	0.89
250	1296.52	1508.92	275. 62	209.34	0.58
300	1292.40	1508.12	266.92	207.75	0.45
350	—	1496.78	—	200.31	—

3.2. Hardness (H) and elastic modulus (E)

For thin films, the underlying substrate properties strongly influence the indentation response and it is difficult to see the intrinsic film properties. One approach for dealing with the substrate influence is to make the indentation small enough to avoid the substrate effect. In practice, this is accomplished by constraining the indentation depth to a small fraction of the film thickness; however, it should still be large enough to effect full plasticity [21]. A commonly accepted rule of thumb suggests that the substrate independent measurements can be obtained if the indentation depth is kept to less than 10 % of the film thickness. Accordingly, nanoindentation characterization of 100 nm films would have to be made at a penetration depth of less than 10 nm. However, accurate measurements at this scale are difficult to be obtained due to vibration, tip rounding effects, difficulties in precise determination of the location of the specimen and incomplete subtraction of the Hertzian behaviour. For purposes of comparison in the following discussion, hardness (H) and elastic modulus (E) values will be considered as representative of the composite film/substrate. The results represent average values of 10 indents on each sample.

Figure 3 shows the hardness (H) and elastic modulus (E) of the DLC films as functions of the substrate negative self-bias voltage. The H and E of the DLC films increase first and then decrease, with increasing substrate negative self-bias voltage from 100 to 300 V. The H and E had a peak value of 17.341 GPa and 161.971 GPa, respectively, at the substrate negative self-bias voltage of 200 V.

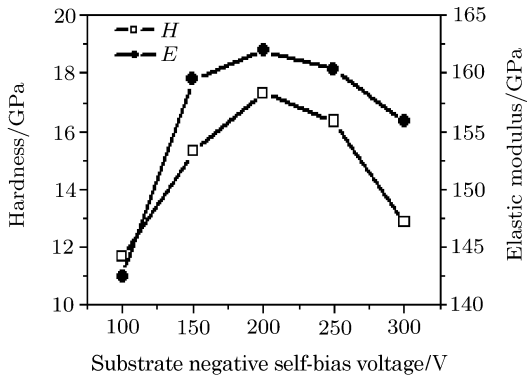


Fig.3. Effects of substrate negative self-bias voltage on the hardness (H) and elastic modulus (E) of DLC films.

The explanation of such a behaviour may be as follows. At low values of self-bias, the increase of hardness is mainly due to the enhanced substrate bombardment by energetic ion species. At higher values of self-bias, films present a graphitic character, with high

concentration of sp^2-bonded carbon. The increase in the deposition temperature due to the ion bombardment leads to the film graphitization, which in turn causes the hardness and elastic modulus to decrease.

Figure 4 presents hardness (H) and elastic modulus (E) values for a series of DLC films, with different Si additions. The hardness of the DLC films decreases slightly from 15.279 to 14.968 GPa with increasing Si target power from 100 to 300 W. The changes of the elastic modulus (E) showed the same tendency of decrease as that of the hardness (H).

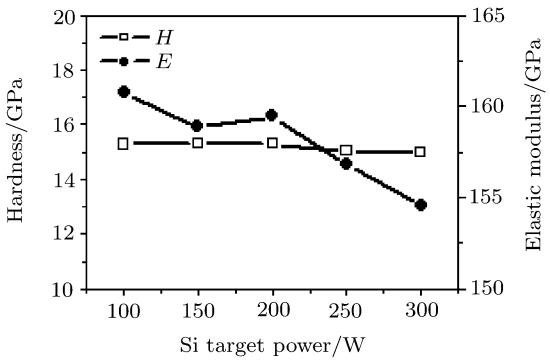


Fig.4. Effects of Si incorporation on the hardness and Young's modulus of DLC films.

When the Si target power is raised, the hydrogen content increases. It seems that Si doping promotes the formation of sp^3-bonding in the DLC films, along with a reduction in hardness. This result is in good agreement with the downshift of the G peak in Raman spectra. The bonding constraints of sp^3-bonded carbon changes by binding more hydrogen, thus relaxes the stress and reduces the hardness and elastic modulus of the DLC films.[22] Silicon incorporation may also increase the number of Si–C and Si–Si bonds. As these are weaker than C–C bonds, it is expected that their presence would further weaken the structural integrity of the films.

3.3. AFM analysis

In order to reveal the surface morphology of the wear tracks in greater detail, AFM imaging was performed with a scan size of 500 nm. The variation of root mean square (RMS) roughness with the substrate negative self-bias voltage for DLC films is shown in Fig.5. The roughness measurement results are shown in Table 4.

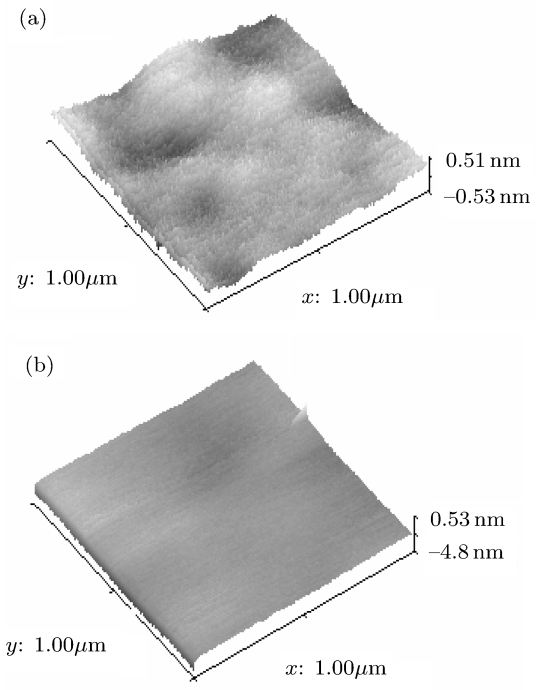


Fig.5. Variation of AFM image of DLC films on stainless steel substrates with Si/SiC intermediate layers for different substrate negative self-bias voltages: (a) 100 V; (b) 200 V.

Table 4. The roughness results of the DLC films with different substrate negative self-bias voltage.

Substrate negative self-bias voltage/V	RMS roughness /nm
100	0.36
200	0.25

The RMS roughness generally decreased with increasing negative bias voltage. The roughness of DLC films deposited under 100 V was 0.36 nm, as shown in Fig.5(a). When the substrate negative self-bias voltage was 200 V, surface was smoothed evidently to an RMS roughness value of 0.25 nm. At higher biases, the kinetic energy of the ions efficiently eliminates voids, asperities and rough particles by higher surface atomic mobility during film growth and preferential sputtering and etching of topographically higher parts of the surface.[23] Hence, smoother surfaces can be achieved at higher bias. The high RMS roughness of DLC prepared at lower bias is due to the formation of small clusters on the surface. The kinetic energy of the ions at a low bias may be insufficient to remove certain asperities and hence, unable to smooth the film surface.

Figure 6 and Table 5 shows the variation of AFM images of the films deposited with different target powers of 100 and 200 W. The roughness of the deposited films was in the range of 0.20–0.18 nm. It can be observed from the figure and the table that the cluster size decreases with increasing target power, which may be attributed to the decreasing number of sp^2 bonded carbon sites, as deduced from the Raman results discussed above. The structural transition from C–C to C–Si bonds also results in relaxation of the residual stress which leads to more even and smoother surface.

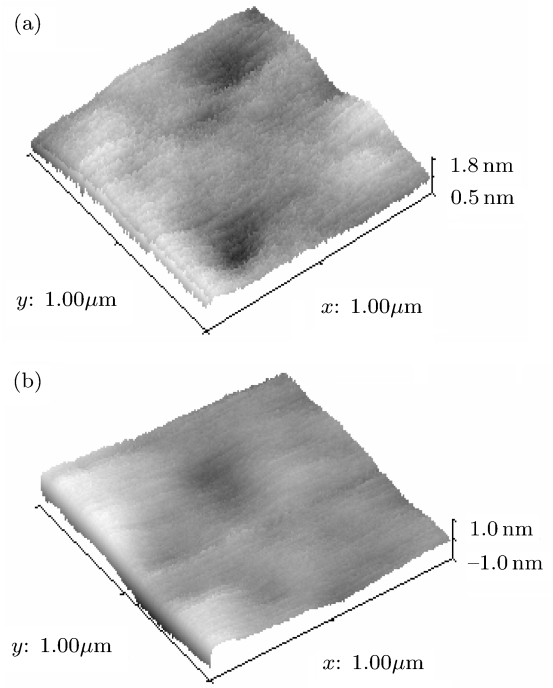


Fig.6. Variation of AFM images of DLC films deposited on stainless steel substrate with Si/SiC intermediate layers at different Si target power: (a) 100 W; (b) 200 W.

Table 5. The roughness results of the DLC films with different Si target power.

Si target power/W	RMS roughness/nm
100	0.20
200	0.18

4. Conclusions

We have investigated the effects of substrate negative self-bias voltage and silicon target power on the microstructure, nanomechanical properties and the film structural morphology of DLC films. Our DLC films were grown on stainless steel substrates successfully with Si/SiC intermediate layers by combining the plasma enhanced sputtering physical vapour deposition (PEUMS-PVD) and microwave electron cyclotron resonance plasma enhanced chemical vapour deposition (MW-ECRPECVD) techniques.

With the increase of substrate negative self-bias voltage, the D and G peak shift to high wave-number and the integrated intensity ratio I_D/I_G increases (in the range of 0.59–1.39). We consider the shift in the position of the G peak and the increase of I_D/I_G ratio in DLC films as evidence, for the development of graphitization in the films. The hardness (H) and elastic modulus (E) increase with the enhanced substrate bombardment by energetic ion species, but decrease with the development of graphitization in the films. Hence, the H and E curves had peak values of 17.341 and 161.971 GPa, respectively, at the substrate negative self-bias voltage of 200 V. As the substrate negative self-bias voltage increases, particle bombardment function was enhanced and sp^3-bond carbon density was reduced, also resulting in a corresponding decrease in roughness.

Silicon doping suppressed the formation of sp^2-bonded carbon and increased the sp^3-bonding and the hydrogen content in the DLC films, along with reduction in the hardness and elastic modulus. The high hydrogen concentration in the DLC films was confirmed by the Raman result. The change of the nanomechanical properties was correlated with the increase in hydrogen content, which enhanced the formation of a polymeric sp^3-bonding structure. The structural transition from C–C to C–Si bonds also resulted in relaxation of the residual stress which led to the decrease of hardness and roughness.

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