Thin Solid Films 519 (2011) 2043–2048

Contents lists available at ScienceDirect

Thin Solid Films

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

Effects of duty cycle and water immersion on the composition and friction performance of diamond-like carbon films prepared by the pulsed-DC plasma technique

F. Zhao [a,b], H.X. Li [a], L. Ji [a], Y.F. Mo [c], W.L. Quan [a,b], Y.J. Wang [a,b], J.M. Chen [a,*], H.D. Zhou [a]

[a] State Key Laboratory of Solid Lubrication, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, PR China
[b] Graduate University of Chinese Academy of Sciences, Beijing 100049, PR China
[c] School of Chemistry and Chemical Engineering, Guangxi University, Nanning 530004, PR China

ARTICLE INFO

Article history:
Received 5 December 2009
Received in revised form 20 October 2010
Accepted 27 October 2010
Available online 3 November 2010

Keywords:
Diamond-like carbon
Pulsed DC Plasma
Raman Spectroscopy
Infrared Spectroscopy
Friction
X-ray photoelectron Spectroscopy

ABSTRACT

Diamond-like carbon (DLC) films were prepared in a pulsed-DC discharged CH_4/Ar plasma. Effects of duty cycle ($[t_{on}/(t_{on}+t_{off})]\times 100\%$) on the composition and properties of DLC films were investigated. In general, the increased duty cycle led to an up-shift of the G peak position, an increase in the I_D/I_G and sp^2/sp^3 ratio, and a reduction of the number of C–H bonds and the film hardness, revealing a graphitization tendency with increasing duty cycle. Tribologically, ultralow and steady friction coefficients (0.005 and 0.008) in dry nitrogen atmosphere were obtained for the films prepared under a duty cycle of 50% and 65%. The unique mechanical property and chemical nature brought by the moderate sp^2/sp^3 ratio and the proper H content were considered to be responsible as the films deposited in this duty cycle range could simultaneously provide the high chemical inertness and the ultrasmooth sliding surfaces required for achieving ultralow friction. In addition, the structure was less vulnerable to water molecules in the case of stewing. The diamond-like nature and the ultralow friction performance were hardly affected even experiencing a 4-month immersion in water.

1. Introduction

Diamond-like carbon (DLC) films prepared from hydrogen-rich CH_4 source gas plasmas have been reported to exhibit an ultralow friction coefficient of 0.001–0.003 and a wear rate of 10^{-9} to 10^{-10} mm^3/Nm in vacuum or dry nitrogen environments [1]. Excellent tribological performance was also shown by our hydrogenated DLC films prepared by the pulse bias-assisted radiofrequency plasma enhanced chemical vapor deposition (RF-PECVD) method. They displayed an ultralow friction coefficient of ~0.006 in both dry N_2 and CO_2 atmospheres [2]. Nevertheless, from the perspective of industrial application, the RF-PECVD method may not be a candidate as competitive as the pulsed direct current (DC) plasma technique. Unlike the RF technique, the pulsed-DC technique could use higher power levels (while simultaneously keeping the average power in an usual range [3]) and does not require matching networks, thus leading to an easy implementation in industrial plasma processing systems and a reduction of the production cost [4–7]. In addition, the pulsed-DC deposition method has been used to deposit DLC films on surfaces with special geometry, e.g., to coat DLC inside the inner wall surface of model dies with holes of 2 and 0.9 mm in diameter and 20 mm in depth [8]. Moreover, DLC films produced from the pulsed-DC PECVD possessed improved mechanical and tribological properties (high adherence and wear resistance, low stress, low roughness, and low friction coefficient), which made them an alternative for use as protective coatings on magnetic storage devices and sliding surfaces [5].

Among others, one key parameter in the pulsed-DC deposition process is the duty cycle (here defined as ([(pulse-on time)/(pulse-on time + pulse-off time)] × 100%), or ($[(t_{on}/(t_{on}+t_{off})]\times 100\%$)). It is a significant and effective factor in controlling the composition (sp^3/sp^2 ratio) and properties (especially the hardness and stress) of the DLC films. After systematically investigating the effect of pulse parameters on the properties of DLC films, Kumar et al. [9] found that DLC films with both low stress and high hardness could be obtained and three factors were responsible: (i) relaxation of adions/adatoms, (ii) control of substrate temperature, and (iii) creation of a hard/soft multilayer structure [9]. All these three factors intimately correlated with the cooling and relaxing effect during the pulse-off period of the pulse plasma discharge (but this effect was absent in the continuous discharge techniques). Similarly, Anders [3] proposed that the pulsed processing was able to produce amorphous carbon film with high sp^3 content by using a suitably low duty cycle since it could keep a small average heat load on the substrate surface and, accordingly, control the substrate heating [10] without affecting the kinetic energy of ions. Effects of the duty cycle on the film structure and properties were also noted in our previous work [11]. It was found that the low pulse duty cycle promoted the formation of fullerene-like structure in the hydrogenated carbon films produced by the pulse bias-assisted RF-PECVD method. In that case, however, the role of the duty cycle was not fully reflected due to the coexistence of the RF power. Hence,

* Corresponding author. Tel.: +86 931 4968018; fax: +86 931 8277088.
E-mail address: chenjm@licp.cas.cn (J.M. Chen).

0040-6090/$ – see front matter
doi:10.1016/j.tsf.2010.10.042

in present work, we synthesized DLC films by using the pulsed-DC method alone and investigated the effect of the duty cycle on the film composition and friction performance in dry nitrogen atmosphere. In addition, in view of the significant effect of water on the hydrogenated structure and friction performance of DLC films [12], 4-month immersion of the sample (with the best lubrication performance) in water was performed, followed by the Raman and friction characterization.

2. Experimental details

DLC films were deposited on polished stainless steel (1Cr18Mo8-Ni5N) substrates and n-type Si (1 0 0) wafers by the pulsed-DC PECVD method. The schematic illustration of the deposition system has been given previously [13]. Driven by a 40-kHz mid-frequency unipolar pulsed-DC power, the cathode (substrate holder) was negatively charged to generate plasma. A schematic diagram of the rectangular waveform of the pulsed-DC power supply is shown in Fig. 1. The duty cycle ($t_{on}/(t_{on}+t_{off})\times100\%$) could be adjusted according to the process requirement. A mixture of methane and argon was used as the source gas, and the pressure was controlled to be constant at 1.5 Pa during deposition. The deposition duration was 60 min, and the thickness for all samples was measured to be 485 ± 10 nm. Detailed deposition parameters are described in Table 1. Prior to deposition, substrates were firstly etched with Ar^+ plasma at a bias voltage of -1000 V for 20 min in order to remove the native oxide layer on the sample surface. Then, a Si adhesive layer of about 200-nm thickness, with a graded intermixed Si–Fe interface, was deposited in order to enhance the film-to-substrate adhesion strength. The detailed Si-interlayer deposition process can be found in Ref. [14].

All samples were analyzed using a Bruker IFS 66v/S Fourier transform infrared (FT-IR) spectrometer. The transmission spectra were taken between 400 and 4000 cm^{-1} with a resolution of 0.23 cm^{-1}. A LabRAM HR800 (HORIBA Jobin Yvon, France) micro-Raman spectrometer operating with 532 nm Ar^+ laser as the excitation source was used to characterize the film structure. The laser beam was focused onto the sample surface using an optical microscope with a magnification of 100× (laser spot size ~1 μm). The acquired Raman spectra were fitted based on Gaussian curve shapes with the curve-fitting software. A PHI-5702 X-ray photoelectron spectroscope (XPS) operating with monochromated Al-Ka irradiation at a pass energy of 29.35 eV was employed to analyze the chemical composition and chemical bond states of the film surfaces, with the binding energy of Au (Au4f: 84.0 eV) as the reference.

The film hardness and elastic modulus values were determined using an Nano-Hardness Tester (MTS Nano Indenter XP), where the maximum indent depth was controlled to be 45 nm (less than 1/10 of film thickness) so as to minimize the effect of the substrate [15], and five repeated indentations were made for each sample. Friction and wear properties of the DLC films were evaluated on a reciprocating-type ball-on-flat CSM tribometer, which was equipped with a chamber where the relative humidity (RH) and gaseous environment could be controlled. Sliding tests were performed in dry nitrogen environment (RH<5%) at an average sliding velocity of 80 mm/s at room temperature. DLC-coated steel balls (12.0 mm in diameter) were used as the counterparts. Tap water was used to immerse the selected DLC film.

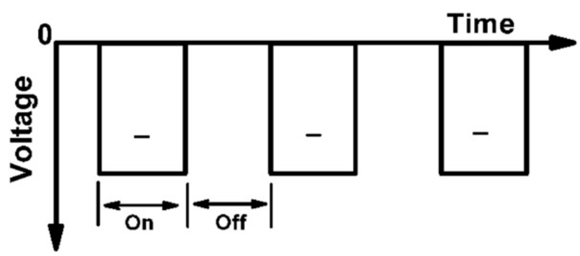

Fig. 1. Schematic diagram of waveform of pulse power supply. Duty cycle $=[t_{on}/(t_{on}+t_{off})]\times100\%$.

Table 1
Deposition parameters for DLC films.

Parameter	Value
Working pressure, Pa	1.5
Mass flow rate of CH_4, sccm	200
Mass flow rate of Ar, sccm	75
Pulse frequency, kHz	40
Pulse voltage, V	−1000
DC bias, V	−200
Duration, min	60
Duty cycle, %	20; 35; 50; 65; 80 (film-1 to film-5)

3. Results and discussion

Fig. 2 gives the FT-IR spectra of five samples. The strong peaks centered at ~2851 cm^{-1} and ~2923 cm^{-1} correspond to the symmetric and asymmetric stretching mode of sp^3 CH_2, respectively. The weak peaks present at ~2874 cm^{-1} and ~2954 cm^{-1} are assigned to the symmetric and asymmetric stretching mode of sp^3 CH_3, respectively. As seen, the peak intensity generally decreases with increasing duty cycle, suggesting a reduction in the number of C–H bonds. Variation of the H content could also be reflected by the Raman spectra since high amounts of H usually lead to a high sp^3 content and a down-shift of the G peak [16], as discussed below.

Raman spectroscopy is a standard non-destructive technique for the characterization of carbon-based materials, and the characteristic Raman spectra can be used to study the structural arrangements of the carbon atoms [17]. Visible Raman spectra of DLC films are dominated by scattering of the sp^2 sites, since the Raman cross section of sp^2 sites is 50–230 times larger than that of the sp^3 sites [16,18]. Usually, the Raman spectra of DLC films are characterized by a G peak around 1550 cm^{-1} and a D shoulder around 1360 cm^{-1} [17]. The G peak is the stretching vibration of sp^2 sites in both rings and chains, while the D peak is due to the breathing mode of those sp^2 sites only in aromatic rings [16]. Although the visible Raman spectra depend formally on the configuration of the sp^2 sites and only indirectly on the sp^3 content, they can still be used to derive the information about the sp^2/sp^3 ratio from I_D/I_G (intensity ratio of the D peak to the G peak) [16–18]. Generally, if the FWHM (full width half maximum) of the G peak exceeds 50 cm^{-1}, the in-plane correlation length L_a (or the diameter of graphitic cluster) would be below 1 nm. And for L_a below 2 nm, the following relationship could be used: $I_D/I_G=cL_a^2$, where c is a constant

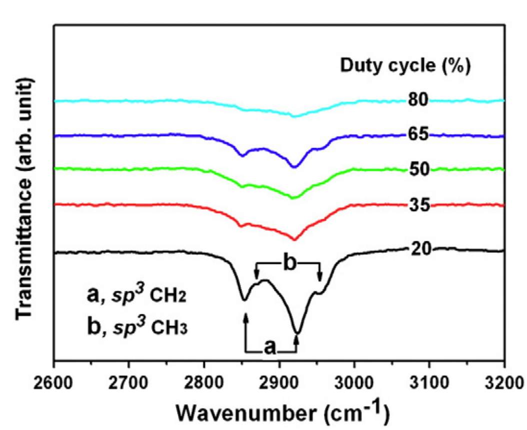

Fig. 2. FT-IR spectra of DLC films.