Heating induced nanostructure and superlubricity evolution of fullerene-like hydrogenated carbon films

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ABSTRACT

Fullerene-like hydrogenated carbon (FL-C:H) films hold superlubricity properties at room condition, which important for saving energy, for engine use, however, high temperature serving (below 500 °C) are needed considering. In this paper, FL-C:H films were annealed with protecting of nitrogen. The tribological test show that all films have superlubricity properties, of which friction coefficient are 0.008 (200 °C), 0.005 (250 °C), 0.004 (300 °C), 0.005 (400 °C), 0.004 (500 °C), respectively. In addition, the hardness is incremental when the annealed temperature increased from 200 to 300 °C, and decremental from 300 °C to 500 °C. Interestingly, the changes of hydrogen content can be neglect in present work. Combined HRTEM, Raman spectra and XPS results, one can speculate that the degree of order for FL-C:H films increase along with the argument of annealed temperature, but competition of growth and ordering of short-chain hydrocarbon and graphene stacks that determine the hardness and H^3/E^2 ratio, which further influences the wear volumes. However, the friction coefficient only depends on curved grahene which can formation scroll graphene between contact surface to low friction force.

1. Introduction

Friction and abrasion are mostly harmful and unavoidable of contacting surfaces in machinery components, but one can try to reduce them via surface modification. A sufficient method is to deposit protective coatings or films on the surface of machinery parts for reducing friction and improving the anti-wear performances [1,2]. Carbon based films have exceptional thermal, optical, mechanical, and electronic properties [3–5]. Specially, diamond-like carbon (DLC) film which illustrates marvelous capabilities such as low friction coefficient, excellent wear-resistance and high chemical inertness, have drawn the attention of science and technology [6–8]. Furthermore, the properties that the deposited process can be achieved in low temperature and can be grown on many substrates, which make DLC films adopt generally in industrial field [9–12]. Furtherly, in order to enhance frictional and mechanical properties of the DLC films, plenty of methods are used such as the doping of metal and nonmetallic elements, heat treatment and adding nanostructures[12−20]. When the nonmetal elements such as nitrogen, sulfur, silicon et al. are doped, DLC films show the low or ultra-

low friction coefficient in special atmosphere [12–14]. And when the metal elements such as Ti, Cr, W et al. are doped, DLC films own better mechanical properties and anti-wear [15–17]. More recently, Zhang et al. have shown that fullerene-like hydrogenated carbon (FL-C:H) films with curved graphene structure stacked hold superelastic and superlubricity properties [18–20]. They further confirmed that superlubricity of such films depend on the formation of onion-like structure in the contact interfaces [18].

However, the superlubricity of FL-C:H films is only determined under room conditions. In actual application, such as in engine, piston rings are working at high temperatures. For the reason, protecting films must be work below 500 °C. As an excellent lubrication films, FL-C:H films have never been discussed of about the structure and tribology properties evolution with temperature vibration. In this paper, the tribological properties of FL-C:H films after annealed treatment are discussed. The mechanisms of anti-friction and wear reduction are elaborated in the aspect of nanostructures and mechanical properties.

2. Experimental

2.1. Films preparation

The films on Si (100) substrates were deposited by plasma enhanced chemical vapor deposition (PECVD) system. Silicon wafers were ultrasonically cleaned in ethanol for 30 min and rapidly put into a vacuum chamber. The substrates were etched in Ar^+ plasma (pulsed frequency: 60 kHz, negative voltage: 980 V and duty cycle: 0.6) within 30 min prior to deposition. The deposited parameters of films were that the negative substrate bias, pulsed frequency, duty cycle and the deposition pressure were 870 V, 60 KHz, 0.6 and 16 Pa, respectively. And the source gas was methane (10 sccm). The films deposition time was three hours.

After the deposited process has completed, the films were annealed in a pipe furnace with protecting of nitrogen. The thermal treatment temperature was set as 200 °C, 250 °C, 300 °C, 400 °C, 500 °C, respectively. The annealed time was thirty minutes and the rate was about 4 °C/min.

2.2. Characterizations of films

The hydrogen content was surveyed by elastic recoil detection (ERD) analysis technology. The mechanical properties of the films were surveyed by a Nano-indentater (Hysitron Ti-950) system. The indentation depth was 50 nm. The structure characters of the films were exhibited by high resolution transmission electron microscope (HRTEM, FEI Tecnai G2 F20 S-TWIN), scanning electron microscopy (SEM, JSM-5601LV), Raman spectroscopy (JobinYvon, Longjumeau, $\lambda = 532$ nm), X-ray photoelectron spectroscopy(XPS, PHI-5702). ERD analyses were performed using the nuclear microprobe of Lawrence Berkeley National Laboratory, University of California, Berkeley (USA). The 2.5 MeV He was used for detection beam and the angle of incidence for dectection beam was 75° with respect to the normal to the sample surface. The protons recoiled from the films were detected by a silicon surface barrier detector (was placed at 30° to the beam). A 13 μm Mylar foil was placed in front of the detector for protection from forward scattering He particles. The HRTEM samples were grown on NaCl wafer in the same deposited conditions with sixty seconds. Straightway the NaCl samples were dissolved in pure water and the thin films were put on Cu grids. Prior the XPS detection, Au thin films about 0.2 nm thick were deposited on the tested carbon film surfaces, which minimize the charging effect, and help to detect the changes of Cls peaks.

2.3. Friction tests

The tribological tests of the films were investigated on a reciprocative ball-on-disc tribotester. The parameters of tribological experiments were that the load, sliding stroke and frequency were 32 N, 5 mm and 2 Hz, respectively. And the temperature and relative humidity (RH) were room temperature and 35% RH in every friction process. The friction couples were steel ball (GCr15, 5 mm). When the friction tests have completed, a MAX 3D three-dimensional surface profiler (ADE, USA) were used to investigate the wear scars and wear volumes.

3. Results and discussion

3.1. The structural characterizations of films

3.1.1. The results of ERD

The hydrogen content of original and annealed films is shown in Table 1. It can be seen that the element hydrogen begins to reduce from FL-C:H films with the annealed temperature of 300 °C. The homologous results can be observed by Vuppuladhadiumet al. [21]. While the

Table 1
The element hydrogen content of original and annealed FL-C:H films.

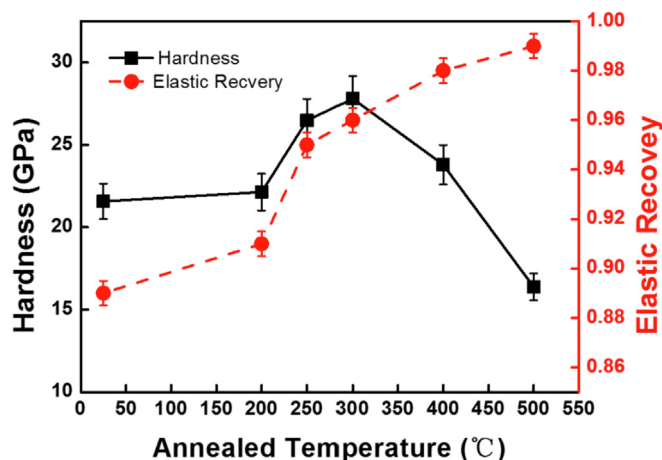|	As-prepared	200 °C	250 °C	300 °C	400 °C	500 °C
The content of H (%)	24.5	24.5	24.5	24.2	23.8	23.3

Fig. 1. The change of hardness and elastic recovery about original and annealed FL-C:H films.

amorphous carbon-hydrogen films which they researched annealed at from 300 to 500 °C, the hydrogen content changes from about 32% to 30%.

3.1.2. The mechanical and frictional properties of films

For the annealed FL-C:H films, the transformation of mechanical performances is fascinating. Fig. 1 illustrates the hardness and elastic recovery change of FL-C:H films under different annealed temperature. Accordingly, the hardness of films is incremental when the annealed temperature increased from 200 °C to 300 °C, and decremental from 300 °C to 500 °C.The films own the highest hardness with the annealed temperature of 300 °C. And the elastic-recovery of films gradually increases as the annealed temperature increasing.

In order to investigate the influence of FL-C:H films friction performances after heat treatment, the frictional test was carried out. The coefficient of friction of original FL-C:H films is the highest (0.009). After annealing of FL-C:H films, the friction coefficients are 0.008 (200 °C), 0.005 (250 °C), 0.004 (300 °C), 0.005 (400 °C), 0.004 (500 °C), respectively (Fig. 2a). In addition, the wear volume for annealed films is 13790 (200 °C), 6621 (250 °C), 5761 (300 °C), 11330 (400 °C), 19440 (500 °C) μm³, respectively. The wear volume of original film is 14460 μm³ (Fig. 2b). Comparably, the wear volume is the lowest at the annealed temperature of 300 °C. Besides, the values of H/E and H^3/E^2 are also investigated (Fig. 2c and d) to help understanding the changes of tribology properties in present study. A tendency for H/E and H^3/E^2 show a contradictory trend, compared with friction coefficient and wear volume.

3.1.3. The results of HRTEM and SEM

Fig. 3 are the results of HRTEM of original film and annealed films. The structure of the FL-C:H film is amorphous carbon structure with curve graphene modified (Fig. 3a). As the temperature gradually rising, the nanostructures become increasingly obvious. Specifically, when the annealed temperature from 200 °C to 300 °C, the curve graphene structures gradually increase (Fig. 3b, c and d). From 400 °C to 500 °C, the nanostructures occur clusters and gathers (Fig. 3e and f). This shows that heat can induce the graphene structures in FL-C:H films. Similarly result has been reported by Zhang et al. [22] that after annealed treatment (300 °C), multilayer graphene nanostructures are emerged in
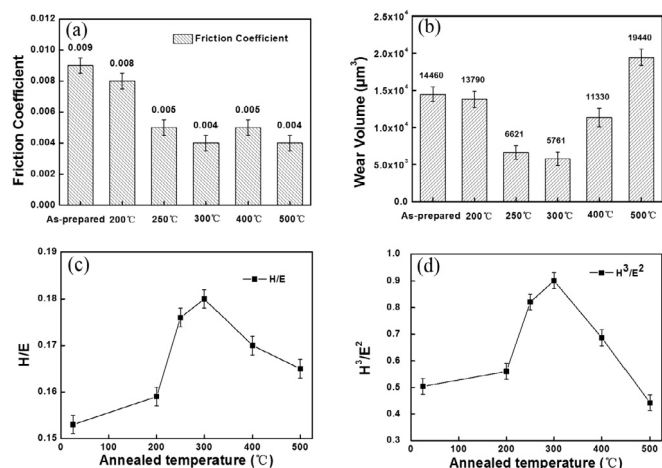
Fig. 2. (a) The average friction coefficient and H/E of FL-C:H films in different annealing temperatures, (b) The value of H/E of FL-C:H films in different annealing temperatures, (c) The value of H^3/E^2 of FL-C:H films in different annealing temperatures. (d) The wear volumes of FL-C:H films in different annealing temperature.
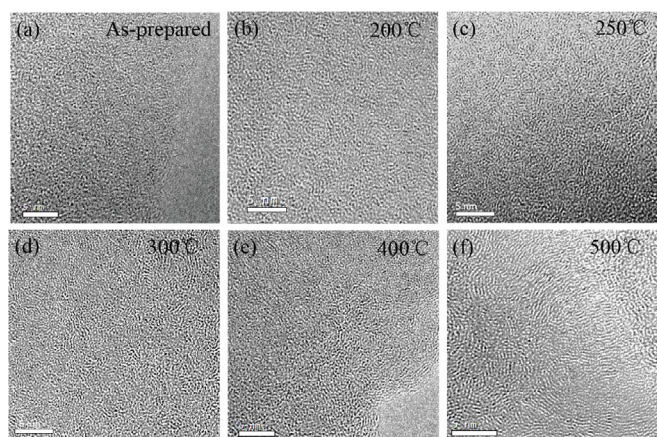

Fig. 3. The HRTEM picture of unannealed (a) and annealed films (b ∼ f).
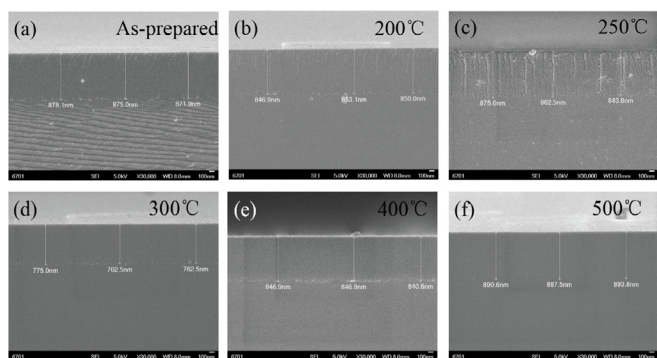

Fig. 4. The SEM images of the films in different annealed temperature.

amorphous matrix. The results are different because the original films they used are amorphous carbon films, but the films discussed in this paper are fullerene-like, that means more graphene fragments are wrapped in carbon matrix. The wrapped graphenes are more easily grow up and ordering than that amorphous structures below 300 °C. Such ordering induces the films densification, which can be proved by SEM images, shown in Fig. 4. Compared the thickness of all films that, one with the annealed temperature of 300 °C is the thinnest and the most compact. With the annealed temperature increased further, the
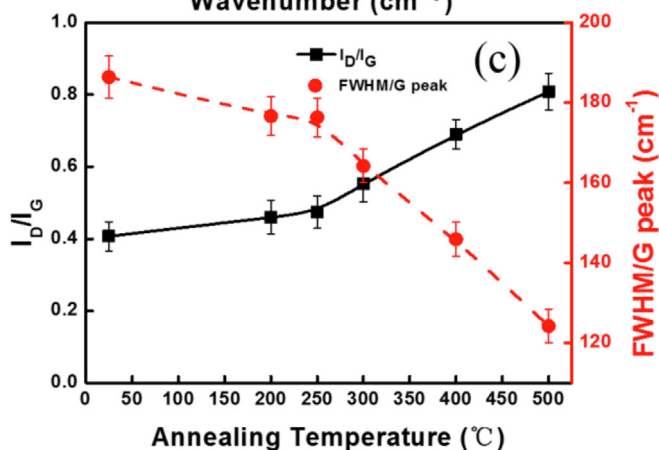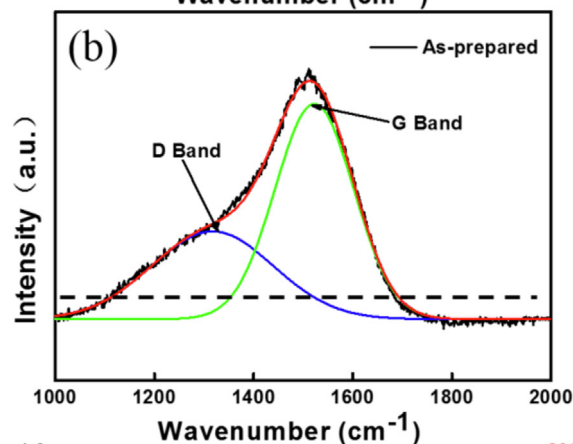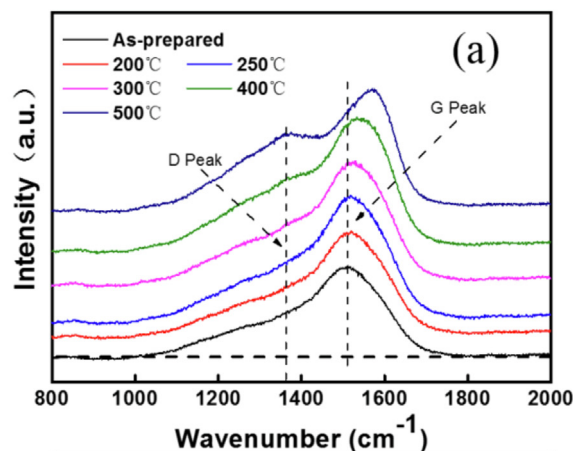

Fig. 5. (a) Raman spectra of FL-C:H films in different annealing temperatures for λ_L = 532 nm, (b) the fitting curve of Raman spectrum for untreated FL-C:H film, (c) the I_D/I_G and the FWHM for G peak of FL-C:H films in different annealing temperatures.

thickness of the films increases linearly. This changes might be attributed the crispation of graphene into clusters and gathers (Fig. 3e and f). To determine this, Raman and XPS could be employed to explore the structure of all films.

3.1.4. The results of Raman and XPS

Raman spectra are an effective testing instrument in carbon materials bonding structures. Fig. 5a is Raman spectra of FL-C:H films in different annealed temperature. From original films to FL-C:H films annealed under temperature of 250 °C, the position of D peak and G peak does not change so much. For FL-C:H films annealed at from 300 to 500 °C, however, the D peak obviously bulges and the G peak shift to high wavenumber. Zhang et al. [23] have shown that the variation of D

peak and G peak means the amorphous carbon structures transform into graphitic structure. Meanwhile, some research indicated that the Red-shifting of the G peak of FL-C:H films annealed at 400 °C and 500 °C also relate to decreasement of the hydrogen content and C-C sp^3 bond [24,25]. However, considering the results of ERD, Red-shifting of the G peak of FL-C:H films has nothing to do with the hydrogen content in this article. Combined HRTEM results, the C-C sp^3 bond evolves into C-C sp^2 bond in the FL-C:H films under heat-treatment, and the less variation of hydrogen content may be the existence of special structure in this films. Besides, the fitting results of D peak and G peak for Raman spectra are shown in Fig. 5b, and the values of I$_D$/I$_G$ are also calculated. Fig. 5c shows the I$_D$/I$_G$ values of FL-C:H films in different annealed temperature. As the annealed temperature increase, the values of annealed films gradually raise. For FL-C:H films, the addition of I$_D$/I$_G$ value implies a raise in the degree of order [23]. Accordingly, the change of the full width at half maxima (FWHM) of G peak in different annealed temperature proves the improvement in the degree of order, too.

Moreover, the analysis of XPS for original and annealed films also reveals the augment of sp^2 cluster. The XPS spectra of films can be appraised by fitting the C1s peak with graphite represented by the sp^2 bond (peak at 284.3 eV), diamond represented by the sp^3 bond (peak at 285.1 eV), and detect represented by the C-O bond [26] (peak at 286.3 eV). Fig. 6a demonstrates the fitted curve of original films. The values of sp^2/sp^3 for FL-C:H films in different annealed temperature are illustrated at Fig. 6b. From original films to annealed temperature of 500 °C, the value of sp^2/sp^3 for FL-C:H films is increasing. The results of Raman and XPS well confirm the thickness variety of thermal treatment films.

3.2. Discussion

One can see from Table 1 that the hydrogen content is nearly unchanged under anneal treatment below 500 °C, the similar results were reported via Vuppuladhadium et al. [21] and Li et al. [27]. They also declared that rapid annealing induced more graphitic. Interestingly, from HRTEM test, more curved graphene are found with increased temperature, which verifies heat treatment can induce growing up of curved graphene. But compared with Zhang et al. [22] that few multilayer graphene was seen after annealing under 300 °C, very different from our work in this paper. One possible reason is that small graphene fragments are wrapped in carbon matrix and short-chain hydrocarbons bond on edges of these graphene which is believed holding mechanical stiffness and high elasticity [28]. So the FL-C:H films show high hardness with super-elastical property [29] (elastic recovery value is 87%). With increase of annealing temperature, seen from Fig. 3, the curved graphene grow up, so the elastic recovery value increase to 99% after annealing at 500 °C (Fig. 1). But the high hardness turn out under 300 °C annealing. The elasticity relates to graphene fragments size and the hardness depends on short-chain hydrocarbons which can prevent graphene slip [30]. Considering the nearly unchanged of hydrogen content (Table 1) and the grown up of curved graphene (Fig. 3), one can speculate that short-chain hydrocarbons could cannibalize each other nearby that not only induce growing up of curved graphene but also

gather chain hydrocarbons. This conclusion can be proved by the bumped of D peak and the red-shift of G peaks (Fig. 5). And the XPS results (Fig. 6) show same trends. Then, one can conclude that the growth of curved graphene with the ordering of chain hydrocarbons contribute to high elastical recovery. Such ordering could also give rise to density the films (Fig. 5) that lead high hardness at 300 °C. But beyond 300 °C, particularly annealed under 500 °C, the G peak position jumps to high wavenumber which confirms that drastic graphitization happens, which looses the matrix of FL-C:H films, accompanying the increasing the film thickness (seen from Fig. 4), so the hardness of the films decreases.

Based on nanostructure evolution of FL-C:H films, the clue of tribology of FL-C:H films to the nanostructure are explored. With increasing of treat temperature, the friction coefficient decrease from 0.009 to 0.005 under 300 °C annealing, beyond this point, the friction coefficient keeps constant. As shown in Fig. 2, all films exhibit super-low friction or superlubricity which is attributed to curly stacked structures [31]. In contrast, the variety of wear volume is inverse relate to hardness. Moreover, A. Leyland et al. [32] proposed that controlling the H/E ratio in frictional progress of nanocomposite coatings is extremely significant for optimal tribological behavior. The value of H/E has a critical role in determining yield pressure and crack propagation. The high value of H^3/E^2 means the improvement of the elastic recovery about the films, and can improve the toughness [33]. In order to research the mechanism, the values of H/E (Fig. 2c) and H^3/E^2 (Fig. 2d) are investigated. In contrast to the frictional coefficient, the films own supreme H/E and H^3/E^2 ratio at the annealed temperature of 300 °C, but the lowest H/E and H^3/E^2 ratio turn out for films un-heat treatment and annealing under 500 °C, respectively. Combined with HRTEM and XPS results, one can understand that trapped curve-graphene which can formation scroll graphene between contact surface to low friction force [29], but competition of growth and ordering of short-chain hydrocarbon and graphene stacks to determine the hardness and H^3/E^2 ratio, and which further influences the wear volumes.

4. Conclusion

The present work of this article was that the microstructure, the mode of bonds, mechanical and frictional performances of the annealed FL-C:H films deposited by PECVD system were investigated. The main conclusions were summed up as following:

(1) In contrast to original FL-C:H films, when the annealed temperature from 200 to 300 °C, the curve graphene structures gradually increase. From 400 to 500 °C, the nanostructures occur clusters and gathers. Moreover, the hydrogen content of FL-C:H films begin to reduce when the annealed temperature higher than 300 °C, but the changes is small.

(2) The hardness of films is incremental when the annealed temperature increased from 200 to 300 °C, and decremental from 300 °C to 500 °C. The FL-C:H films are the most compact at the annealed temperature of 300 °C according to the result of SEM. In addition, the elastic recovery of films gradually increases as the annealed temperature increasing.

(3) Raman and XPS reveal that the degree of order for FL-C:H films increase along with the argument of annealed temperature (200–500 °C). Moreover, the C-C sp^2 content raises and the C-C sp^3 content reduces. The films begin graphitizing as the temperature of 500 °C.

(4) After friction test, the heat treatment films at 300 °C have optimal anti-wear and friction-reducing action. The trapped curve-graphene which can formation scroll graphene between contact surface to low friction force, but competition of growth and ordering of short-chain hydrocarbon and graphene stacks to determine the hardness and H^3/E^2 ratio, and which further influences the wear volumes.
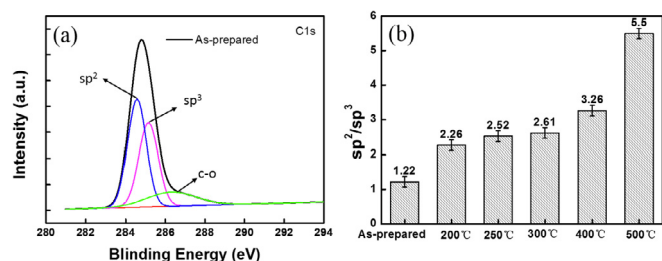

Fig. 6. (a) The fitting curve of XPS spectrum for untreated FL-C:H films, (b) the sp^2/sp^3 of FL-C:H films in different annealing temperatures.

Acknowledgements

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