Multiscale frictional behaviors of sp² nanocrystallited carbon films with different ion irradiation densities

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Received: 20 February 2020 / Revised: 28 March 2020 / Accepted: 02 April 2020
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Abstract: sp² nanocrystallited carbon films with large nanocrystallite sizes, smooth surfaces, and relative high hardness were prepared with different ion irradiation densities regulated with the substrate magnetic coil current in an electron cyclotron resonance plasma sputtering system. Their multiscale frictional behaviors were investigated with macro pin-on-disk tribo-tests and micro nanoscratch tests. The results revealed that, at an ion irradiation density of 16 mA/cm², sp² nanocrystallited carbon film exhibits the lowest friction coefficient and good wear resistant properties at both the macroscale and microscale. The film sliding against a Si₃N₄ ball under a contact pressure of 0.57 GPa exhibited a low friction coefficient of 0.09 and a long wear life at the macroscale. Furthermore, the film sliding against a diamond tip under a contact pressure of 4.9 GPa exhibited a stable low friction coefficient of 0.08 with a shallow scratch depth at the microscale. It is suggested that sp² nanocrystallites affect the frictional behaviors in the cases described differently. At the macroscale, the contact interface via the small real contact area and the sp² nanocrystallited transfer layer dominated the frictional behavior, while the sp² nanocrystallited structure in the film with low shear strength and high plastic resistivity, as well as the smooth surface morphology, decided the steady low nanoscratch properties at the microscale. These findings expand multiscale tribological applications of sp² nanocrystallited carbon films.

Keywords: macro-tribology; micro-tribology; sp² nanocrystallite; carbon film; ion irradiation density

1 Introduction

Carbon films show good tribological properties, for example, amorphous carbon has a low friction coefficient owing to sp² carbon lubrication [1], and tetrahedral amorphous carbon has low wear owing to its high sp³ content [2]. Recently, nanocrystallited carbon films for tribo-applications have been intensively studied because adjustable nanostructures can strongly affect the overall behavior of the films [3–8]. Fullerene-like nanostructure can restrain dislocation migration and aid in stress relaxation to enhance the mechanical and tribological properties of carbon films [3–5].

Graphene nanocrystallite can reduce the friction coefficient [6] of carbon films owing to the low shear force between adjacent graphene layers [7] and increase their elastic recovery and hardness owing to the cross-linked structure between the graphene sheets [8].

Furthermore, with the development of micro- and nanodevices, the influence of scale on tribological behaviors has become important [9, 10]. For macroscale tribological applications, amorphous carbon films exhibited a friction coefficient of about 0.2 when sliding against ceramic balls [11], and recently, transfer film formation and the transformation...
of the nanostructure on the contact area resulted in an even lower value [12–18]. First, forming a transfer film can effectively reduce friction [14–16], and wear was severely reduced after transfer films covered the contact area [17]. Second, the most common nanostructure transformations, such as graphitization, during the friction process of carbon films can also reduce friction, because sp³-to-sp² transition contributes to shear-induced stress relaxation, and sp² graphite crystallite on the contact area is easy to shear [3, 4, 18]. Therefore, a transfer layer is required to achieve a low friction coefficient and prominent mechanical behaviors to ensure suitable contact pressure at the macroscale. For tribological applications at the microscale, the mechanism of low friction coefficient is to reduce the overall strength of the contact interface [19–25]. Good mechanical properties contribute to nanoscratch resistance [20]; for example, the hardness prevents scratching and elasticity helps the film recover from deformation [21, 22]. Low surface roughness also plays an indispensable role in achieving low and stable friction [23, 24], and the ratio of roughness to the penetration depth during a nanoscratch test had a significant effect on the friction coefficient [25]. Therefore, a film should have a nanostructure with a low shear strength, smooth surface, and good plasticity resistance to reduce the shear force at the microscale.

For multiscale tribo-applications, nanocrystallited carbon films prepared by an electron cyclotron resonance (ECR) plasma sputtering system show remarkable mechanical and tribological behaviors [26, 27]. Electron irradiated carbon films exhibited a larger nanocrystallite size, a low friction coefficient of 0.03, and long wear life at the macroscale [6]. Ion irradiated carbon films with different energies can induce the formation of nanocrystallites with high mechanical properties and low nanoscratch depths [28]. However, the electron irradiated ones were too soft to exhibit deep nanoscratch depths at the microscale [29], while the ion irradiated ones with an ion etching effect with different ion irradiation energies normally exhibit higher friction coefficients at the macroscale [26]. As a result, it is difficult to find proper nanocrystallited carbon films exhibiting good frictional behaviors at both the macro and micro scales. It has been found that, beside ion irradiation energy, the ion irradiation density is also a very important factor affecting the nanostructure of carbon films [30]. Therefore, to solve the ion etching effect, carbon films with sp² nanocrystallites were prepared with low ion irradiation energy and adjustable ion irradiation density, and the ion irradiation density was controlled with a substrate magnetic coil current. The macro pin-on-disk tribological properties and the micro nanoscratch frictional behaviors of the films were investigated, and an sp² nanocrystallited carbon film with a large nanocrystal size, smooth surface, and high hardness showed potential for multiscale tribo-applications.

2 Experimental

2.1 Film preparation by regulating the ion irradiation density

The ion irradiation density during the film preparation process was regulated by the mode of the magnetic field in the ECR plasma system, which is shown in Fig. 1. The magnetic flux was controlled by the left target magnetic coils ($t_I$) and the right substrate magnetic coil ($s_I$), as shown in Fig. 1(a). In the system, plasma was generated at the ECR plane, where the magnetic field is 875 G. As $s_I$ was adjusted from 0 to 48 A, the divergent magnetic induction lines became mirror confined. A gaussmeter was used to measure the magnetic flux, as shown in Fig. 1(b). Owing to the effect of the target magnetic coils current, the ECR plane on the left side formed near the target. As the substrate magnetic coil current increased, the magnetic flux gradually increased, and the ECR plane formed near the substrate when $s_I$ reached 40 A. With an increase in the magnetic flux near the substrate, a greater amount of argon gas can be ionized, which can increase the ion irradiation density.

By regulating the mode of the magnetic field, the sp² nanocrystallited carbon films were prepared as follows. The chamber was pumped to a high vacuum of $10^{-5}$ Pa; then, argon gas was inflated into the chamber to maintain a working pressure
of 0.04 Pa. Plasma was generated with microwave power of 700 W, $I_t$ of 32 and 34 A, and $I_s$ ranging from 0 to 48 A. When the plasma stabilized, the silicon substrate (p-type <100>, 25 mm × 25 mm) was cleaned with ion sputtering for 3 min, and the bias applied on the substrate was −50 V. After that, the cylindrical glassy carbon target was sputtered with a bias of −500 V, and carbon films were deposited with substrate bias of −20 V to attract argon ions. With low energy ion irradiation, the films can be grown without the ion etching effect [28]. The density was adjusted by the substrate magnetic coil. The films were deposited with 30 min, and the thickness was about 110 nm. The ion irradiation density was calculated as the quotient of the current flowing through the substrate and the substrate area, and the results was shown in Table 1. The ion irradiation density increased from 1.28 to 26.97 mA/cm² as the current increased from 0 to 48 A.

### 2.2 Film characterization

The Cs-corrected high-resolution transmission electron microscope (HRTEM, Thermo Fisher Scientific, Titan3 Themis G2) was used to observe and analyze the nanostructure of the carbon films. An electron acceleration voltage of 80 kV was used to ensure the nanostructure did not sustain high energy electron beam irradiation damage. The cross-sectional views were obtained by focused ion beam (Thermo Fisher, Scios) milling. The Pt layer was deposited on the film surface before milling. The plan views were obtained by scratching the carbon films surface and transferring the flakes onto a copper micro grid. The electron energy-loss spectroscopy (EELS, Gatan, Quantum ER/965) spectra were obtained in the scanning transmission electron microscopy (STEM) mode operated at 80 kV. The energy dispersion was set to 0.05 eV/channel with a 2.5 mm aperture, and the collection angle was set to 3.6 mrad. The EELS signals for carbon K edge were acquired by subtracting a power-law background. The Raman spectrometer (Raman, HORIBA, LabRAM HR Evolution) was used to further analyze the average size of the nanocrystallites in the carbon films. The 532 nm laser was adopted, focused to 1 μm in diameter by using a 100× objective, and the laser power was kept at 0.1 mW to avoid surface damage. The Raman spectra between the 1,100 and 3,500 cm⁻¹ shifts can be acquired. An atomic force microscope (AFM, Bruker, Dimension Edge) with a silicon scanning probe with a tip radius of 2 nm acquired the surface morphologies of the carbon films by scanning a 1 μm × 1 μm area. The elastic modulus and hardness were tested by the nanoindentation method (Bruker, TI 950), and a diamond probe with a tip radius of 300 nm was used as the indentation tip. To avoid the substrate effect and obtain a deeper indentation depth, a proper indentation load of 600 μN.

### Table 1 Change in ion irradiation density with $I_s$.

| $I_t$ (A) | $I_s$ (A) | Ion irradiation density (mA/cm²) |
|----------|----------|---------------------------------|
| 32 & 34  | 0        | 1.28                            |
| 32 & 34  | 10       | 4.13                            |
| 32 & 34  | 20       | 8.52                            |
| 32 & 34  | 30       | 15.94                           |
| 32 & 34  | 40       | 24.18                           |
| 32 & 34  | 48       | 26.97                           |

Fig. 1 (a) Schematic of sample preparation and (b) transformation of the magnetic induction lines while regulating the substrate magnetic coil current.
was used.

2.3 Friction tests

At a macroscale, the friction test was performed on the pin-on-disk tribometer. Si3N4 balls with a radius of 3.17 mm were employed as the pin. The loads were 1 and 2 N, and the initial Hertz contact pressures were calculated as 0.41–0.57 GPa. The rotary speed was 180 rpm and the track diameter was 3.2 mm, resulting in a sliding linear velocity of 30.2 mm/s. At a microscale, the fiction test was performed on the TribolIndenter (Bruker, TI 950) with a diamond probe (300 nm tip radius). The loads were 200 and 500 μN in the constant load mode, and 0–1,000 μN in the ramp scratch mode. The initial contact pressure was calculated by dividing the load by the scratch area, which was calculated from the scratch width and depth, and it was 1.6–5.8 GPa. The scratch velocity was 0.67 μm/s. The multiscale sliding tests were both performed in ambient air at a room temperature of 22 °C and relative humidity of 55%–60%.

3 Results and discussion

3.1 sp² nanocrystallite structure

Figure 2 shows the TEM images of the carbon films prepared with different ion irradiation densities. Figures 2(a)–2(c) exhibited the plan view TEM images of the carbon films prepared with $I_s$ of 0, 30, and 48 A, respectively. sp² nanocrystallites can be directly observed in the images, and the fast Fourier transformation (FFT) in the upper-right corner also

![Fig. 2](image-url)
revealed two white rings, which indicated the presence of an ordered nanostructure in the carbon films. Figure 2(d) is the cross-sectional view of carbon film with \( I_s \) of 0 A. The thickness of the film was 109 nm, and the sp\(^2\) nanocrystallite grew in vertically alignment with the substrate. From the high magnification images of the cross-sectional view, it can be seen that the sp\(^2\) nanocrystallites uniformly grow in the carbon films from the substrate to the top surface.

To evaluate the variation in sp\(^2\) hybridization with different ion irradiation densities, the core loss EELS spectra of the carbon films were acquired, and the results are shown in Fig. 2(e). A representative spectrum for the film prepared with \( I_s \) of 30 A, which exhibited a \( \pi^* \) peak around 285 eV and a \( \sigma^* \) peak around 292 eV, is shown in the upper-right corner. The percentage of sp\(^2\) can be qualitatively compared by the ratio of area (\( \pi^* \)) to area (\( \pi^* + \sigma^* \)) [31]. A 5 eV window (283–288 eV) was taken as the data range of the \( \pi^* \) peak, and a 20 eV window (283–303 eV) was taken as the range for the \( \pi^* + \sigma^* \) peaks in carbon K-edge. The results revealed that the percentage of sp\(^2\) decreased as \( I_s \) increased from 0 to 30 A and then increased when \( I_s \) was larger than 30 A. The lowest percentage of sp\(^2\) in the carbon film was achieved with \( I_s \) of 30 A. The Raman spectra were obtained and used to further analyze the nanostructure in the carbon films, and the results are shown in Fig. 2(f). A demonstration of peak fitting is shown in the lower-right corner for the film prepared with \( I_s \) of 48 A. The D band around the 1,340 cm\(^{-1}\) shifts and the G band around the 1,590 cm\(^{-1}\) shifts were fitted with a Lorentzian peak and a Breit–Fano–Wagner (BFW) peak, respectively. The ratio of the intensity of the D band and G band (\( I_D/I_G \)) can be obtained, and the following function could be used to calculate the mean nanocrystallite size \( (L) \) in the carbon films [32]:

\[
\frac{I_D}{I_G} = C(\lambda) \cdot \frac{L}{\lambda}
\]

where \( C(\lambda) \) is a constant value that depends on the wavelength of Raman laser, which is 0.55 nm\(^{-1}\) when a 532 nm laser is used. The results revealed that the mean nanocrystallite size increased from 0.88 to 1.21 nm with an increase in \( I_s \). Through the above observation and analysis, sp\(^2\) nanocrystallited carbon films with different contents of sp\(^2\) and sp\(^3\) hybridizations and different nanocrystallite sizes were prepared by changing the ion irradiation densities. During the film deposition, the ion irradiation energy was fixed to 20 eV, which indicates the films were grown with the low energy ion excitation effect [28]. On the other hand, to prevent the heating effect that compromises sp\(^2\) nanocrystallite formation, the temperature was monitored, and it was much lower than the onset temperature of 200 °C for the sp\(^3\)-to-sp\(^2\) conversion process [33]. Therefore, the structural difference was due to the ion irradiation density. On one hand, nanocrystallites easily formed at higher densities [30]. With an increase in ion irradiation density, the density of the excited atoms increased. Once one excited carbon atom encountered another nearby carbon atom, the stable sp\(^2\) bonded structure formed along the existing nanocrystallite direction, which could have resulted in larger sp\(^2\) nanocrystallite in the carbon film. On the other hand, as more ions irradiated on the growing surface, the compressive stress in the film increased, and the incident ions compressed a low density sp\(^2\) network into a higher density sp\(^3\) network [34]. As a result, the faction of sp\(^3\) hybridizations increased in the film. However, when \( I_s \) increased to larger than 30 A, the fraction of sp\(^2\) hybridizations increased. From Fig. 1, it is known that when \( I_s \) reached 40 A, the ECR plane formed near the substrate, which indicated that electron activity had been enhanced. In this case, for films that are grown at high temperatures, thermal spikes may have annealing effects on the formation of larger sp\(^2\) nanocrystallites with more sp\(^3\) hybridizations in the films.

### 3.2 Surface morphology and mechanical behavior

The surface morphology and surface roughness of the carbon films were obtained by using the AFM. As shown in Fig. 3(a), the surface roughness exhibited two different ranges: when \( I_s \) was below 30 A, the surface was flat with several domes, and \( Ra \) was between 0.17 and 0.36 nm. Then, the surface roughness increased sharply to 1.44–1.50 nm when \( I_s \) increased to 40 and 48 A, and the surface showed intensively distributed peaks. During film growth, the ion irradiation energy was important, as the energy dissipation can affect the roughness [35].
The sp² nanocrystallite carbon films were all prepared with a low ion irradiation energy of 20 eV, which means that surface flattening was due to local dissipation of the incident ions rather than physical etching. As a result, the surface roughness was nearly the same when $I_s$ was below 30 A. However, when $I_s$ was 40 and 48 A, the electron activities near the substrate were enhanced as the magnetic field was mirror confined, and the surface roughening was accompanied by structural nanocrystallinity at higher temperatures.

The mechanical behaviors of the carbon films were obtained by using the Triboindenter. To prevent occurrence of the substrate effect, an indentation load of 600 μN was used. The elastic modulus and hardness were calculated with the method proposed by Oliver and Pharr [36], and the results are shown in Fig. 3(b). The elastic modulus and hardness gradually increased with an increase in $I_s$ and reached maximum values when the current was 30 A. It was speculated that the mechanical behaviors of the carbon films are impacted by the percentage of sp³. From the EELS results, the percentage of sp³ was highest when $I_s$ was 30 A, and the carbon film showed the highest elastic modulus and hardness correspondingly. In addition, the ratio of $H^3/E^2$ is a very important parameter that reflects the resistivity of the film to plastic deformation [37]. The results in Fig. 3(b) revealed that the film prepared with $I_s$ of 30 A had the highest value of $H^3/E^2$, which indicated that the film had good elastic recovery to resist the plastic deformation.

### 3.3 Macroscale frictional behaviors

The macroscale frictional behaviors of the carbon films were obtained by using the pin-on-disk tribometer. Figure 4 shows the frictional curves of three carbon films with $I_s$ of 10, 30, and 48 A under a load of 1 N. The stable stage during the process was used to calculate the friction coefficient, as marked in the figure, and the wear life was represented by sliding circles before the carbon film was worn out, which could be obtained when the friction coefficient suddenly increased to about 0.6 or largely fluctuated. When $I_s$ was 10 A, the friction coefficient of the film was high, and the film was worn out before 20,000 rounds. For the films with $I_s$ of 30 and 48 A, after the running-in process, the friction force stabilized, and the mean friction coefficients were calculated as 0.10 and 0.15, respectively. The wear lives of the films both exceeded 20,000 rounds. Figure 5 summarizes the friction coefficient and the wear life for all the samples under loads of 1 and 2 N. The friction coefficient can touch the bottom when the current is 30 A for both the 1 and 2 N loads, and the lowest friction coefficient, 0.09, was achieved with the load of 2 N. The wear life first increased with an increase in $I_s$ and stabilized after $I_s$ of 20 A, which got a remarkable promotion with 100 times than that of $I_s$ of 0 A.

To analyze the contact interface, which mainly affected the macroscale tribology properties, the optical images on the contact area of the ball surfaces at different sliding circles for the films in Fig. 4 were obtained and showed in Fig. 6. For the film with $I_s$ of 10 A, the contact area marked in Figs. 6(a)–6(c) increased with sliding rounds, and when the film was worn out before 20,000 rounds, a large area of carbon films could be observed on the ball surface. For the films with $I_s$ of 30 and 48 A,
the contact area increased before the first 10,000 rounds, and then barely changed. It was found that the carbon film with $I_s$ of 30 A has the smallest contact area from 5,000 to 20,000 rounds. Therefore, the shear strength could be the smallest among all of the films, which results in the lowest friction coefficient. The other main factor that could affect the shear strength was the transfer film. From the images in Fig. 6, the transferred wear materials mainly accumulated around the contact edge and the transfer film formed within the entire contact area only when the film with $I_s$ of 30 A slid at 20,000 rounds. To investigate the nanostructure evolution in the transferred wear films, the Raman spectra of the marked positions in the transfer film were obtained and are showed in Fig. 7(a). Compared with the original Raman spectra of the carbon films, the D peak separated from the G peak after sliding at positions P1–P3, which meant the presence of the carbon nanocrystallite. And the mean nanocrystallite size increased from 1.14 to 1.24 nm and from 1.21 to 1.23 nm for the films with $I_s$ of 30 and 48 A, respectively. Although the size of the sp² nanocrystallite increased during the sliding, the entire transfer film in the contact area formed with difficulty, and it was suggested that the contact area mainly affected the tribological properties. By using the measured elastic modulus in Fig. 3(b), the Hertz contact areas ($A_c$) at the friction interface were calculated by the following function [38]:

$$A_c = \pi \cdot \left( \frac{3WR}{4E^*} \right)^2$$

$$\frac{1}{E} = \frac{1 - \nu_1^2}{E_1} + \frac{1 - \nu_2^2}{E_2}$$

where $W$ is the load; $R$ is the radius of the Si$_3$N$_4$ ball; $E^*$ is the equivalent elastic modulus, which is
calculated by Eq. (3); $\nu_1$ is the Poisson ratio of the Si$_3$N$_4$ ball; $\nu_2$ is the Poisson ratio of the carbon film; $E_1$ is the elastic modulus of the Si$_3$N$_4$ ball; and $E_2$ is the elastic modulus of carbon film.

The calculated results of the Hertz contact areas and the real contact areas after 5,000 rounds are shown in Fig. 7(c). The real contact area was measured with the wear track rather than the transfer film, because the wear debris may accumulate around the contact area in the transfer film, as shown in Figs. 7(d) and 7(f). The trend of the experimental results was nearly the same with the calculated ones, and the contact areas of the carbon films with different ion irradiation densities decreased first, and then increased. The contact area can touch the bottom when $I_s$ was 30 A. As shown in Fig. 7(e), with a smaller contact area, the shear strength at the contact interface decreased, which resulted in a low friction coefficient [39]. With regard to the wear life of the carbon films, it was suggested that a low contact area with a low friction coefficient decreased the wear.

3.4 Microscale frictional behaviors

The microscale frictional behaviors of the carbon films were obtained by using the Triboindenter. Figure 8(a) shows the frictional curves of the films with $I_s$ of 0, 30, and 48 A tested at constant loads of 200 and 500 $\mu$N, and the ramp load of 0–1,000 $\mu$N, respectively. When the load was 200 $\mu$N, all the scratch processes were stable, and the carbon film with $I_s$ of 30 A had the lowest friction coefficient. When the load increased to 500 $\mu$N, all the scratch processes were stable, and the carbon film with $I_s$ of 30 A had the lowest friction coefficient. When the load increased to 500 $\mu$N, all the scratch processes were stable, and the carbon film with $I_s$ of 30 A had the lowest friction coefficient. When the load increased to 500 $\mu$N, all the scratch processes were stable, and the carbon film with $I_s$ of 30 A had the lowest friction coefficient. 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When the load increased to 500 $\mu$N, all the scratch processes were stable, and the carbon film with $I_s$ of 30 A had the smallest nanoscratch depth.
Fig. 8 (a) Nanofriction curves with $I_s$ of 0, 30, and 48 A at the constant loads of 200 and 500 µN, and ramp load of 0–1,000 µN. (b–d) Schematics of the frictional mechanisms for the three films shown in (a).

Fig. 9 Trends of the friction coefficient and nanoscratch depth with $I_s$ at loads of 200 and 500 µN.

Three schematics were drawn to illustrate the mechanism of the microscale frictional behaviors of the sp$^2$ nanocrystallite carbon films, which corresponded to the three carbon films in Fig. 8(a), as shown in Figs. 8(b)–8(d). At the microscale, with nanoscratch tests, an apparent difference was that stick-slip friction was observed rather than stable macro frictional behavior. The critical load for the appearance of stick-slip was quite different. The occurrence of stick-slip friction can be influenced by the nanostructure [40] and surface roughness [41] of the film. First, the hybridization of carbon atoms with unsaturated bonds can lead to the formation of covalent bonds between the contact surfaces, which results in stick-slip friction. Second, the sp$^2$ nanocrystallite with cross-linking and sp$^3$ hybridizations can increase the hardness of the film, which reduces the adhesion at the contact interface with decreased contact area [28]. For the sp$^2$ nanocrystallized carbon films with different ion irradiation densities, the resistivity to plastic deformation is smaller for films with $I_s$ of 0 A than for films with $I_s$ of 30 A. Moreover, the tip can be easily trapped by the film during sliding processes with high interfacial shear strength (Fig. 8(b)), resulting in a larger degree of stick-slip friction with a high friction coefficient. For the film with $I_s$ of 30 A, as shown in Fig. 8(c), it had a higher elasticity and the resistivity of plasticity, which finally resulted in a more stable frictional behavior, higher critical load, and smaller degree of stick-slip friction during the sliding process. On the other side, the film with $I_s$ of 48 A had a rougher surface, and the asperities interlocked at the contact interface, as shown in Fig. 8(d). As a result, the motion inhibited by the asperities increases the stick-slip friction of the film.

The frictional strength is governed by the resistance to shear, and the overall interfacial shear strength
is determined by the real contact area, the shear strength, and the surface roughness [41]. For diamond-like carbon films scratched with the diamond tip, the friction coefficient could vary from 0.08 to 0.65 with an increase in load and normally has an average of about 0.2 [11, 24]. The carbon film prepared with $I_s$ of 0 A, which had very small sp$^2$ nanocrystallites exhibited the nanoscratch friction behavior just like the amorphous carbon films. However, for the sp$^2$ nanocrystallized carbon film prepared with $I_s$ of 30 A, the contact area receded with the higher resistivity to plastic deformation, and the larger sp$^2$ nanocrystallites in the films contributed to the low shear strength at the contact interface, which resulted in a very stable low friction coefficient of about 0.08. For the nanoscratch test, the wear of the sp$^2$ nanocrystallized carbon film was evaluated by considering the nanoscratch depth, and the film with $I_s$ of 30 A had the smallest nanoscratch depth, which may be due to the high hardness and resistivity of the film to plastic deformation. Furthermore, the nanofatigue property also reflects the wear resistance of carbon films, which has an effect on the hardness and the elastic modulus of the film [42, 43]. It was suggested that the sp$^2$ nanocrystallized carbon film with $I_s$ of 30 A may also exhibit long nanofatigue life owing to the high faction of sp$^3$ in the film. To sum up, at the microscale, the nanoscratch frictional behavior was mainly dominated by the sp$^2$ nanocrystallized structure in the film and the surface morphology of the film.

Based on the above experiments and analyses, for the sp$^2$ nanocrystallized carbon films prepared with different ion irradiation densities, the trend of the friction coefficient at the macroscale was almost same as that at the microscale. The sp$^2$ nanocrystallized carbon film with a large nanocrystal size, smooth surface, and relative high hardness prepared with an appropriate ion irradiation density had a stable low friction coefficient and multiscale wear resistance. The films could be explored in a multiscale range of applications as solid lubricating layers and wear resistant protective layers.

4 Conclusions

In summary, sp$^2$ nanocrystallized carbon films were prepared with different ion irradiation densities regulated by $I_s$ in the ECR plasma sputtering system. The nanostructure and the surface properties varied with the ion irradiation density, and sp$^2$ nanocrystallized carbon films prepared with an appropriate ion irradiation density of 16 mA/cm$^2$ had a large nanocrystal size, smooth surface, and relative high hardness and plastic resistivity. The multiscale frictional behaviors were investigated with macro pin-on-disk tribo-tests and micro nanoscratch tests. The results revealed that the sp$^2$ nanocrystallized carbon films exhibited low friction coefficients and good wear resistances in ambient air at both the macro and micro scales. A low friction coefficient of 0.09 and a long wear life at the macroscale were achieved when the Si$_3$N$_4$ ball slid against the film at a contact pressure of 0.57 GPa. Furthermore, a stable low friction coefficient of 0.08 with a shallow scratch depth at the microscale was obtained when the film slid against a diamond tip under contact pressure of 4.9 GPa. It is suggested that the sp$^2$ nanocrystallites affect the frictional behaviors in the cases described above differently. At the macroscale, the contact interface via the small real contact area and the sp$^2$ nanocrystallized transfer layer dominated the frictional behaviors, while the sp$^2$ nanocrystallized structure in the film with low shear strength and high plastic resistivity, and the smooth surface morphology determined the steady low nanoscratch properties at the microscale. These findings enrich understanding of the friction mechanism at the multiscale and provide a new way to fabricate sp$^2$ nanocrystallized carbon films that can be explored in a multiscale range of applications as solid lubricating layers and wear resistant protective layers.

Acknowledgements

The authors wish to thank the staff at the Electron Microscope Center of Shenzhen University for their assistance with the HRTEM observations and EELS tests. The research work was supported by the National Natural Science Foundation of China (No. 51975382), Natural Science Foundation of Guangdong Province (No. 2018A030313908), and Shenzhen Fundamental Research Free-exploring Project (JCYJ20170817100822005).
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