In-situ TEM studies on stick–slip friction characters of sp^2 nanocrystallited carbon films

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Abstract: Carbon films with two different kinds of sp^2 nanocrystallited structure were investigated to study the stick–slip friction with the *in-situ* and *ex-situ* tests. *In-situ* transmission electron microscope (TEM) observation and nanofriction tests revealed that the origins of stick and slip varied with shear stress and film deformation. At the stick stage, shear stress gradually increased with the contact strengthened until reached the shear strength to break the interfacial adhesion; at the slip stage, the shear stress decreased and accompanied with film deformation. During the sliding process, adhesive deformation resulted in the large stick–slip step while ploughing deformation led to a smoother step. *Ex-situ* nanofriction tests on a series of sp^2 nanocrystallited carbon films with different irradiation energies showed the expected sliding behavior with the *in-situ* results. This study first clarified the mechanism of stick–slip friction with the *in-situ* TEM observation, which plays the important role for the micro and nano application of sp^2 nanocrystallited carbon films.

Keywords: carbon films; stick–slip; contact interface; deformation; *in-situ* transmission electron microscope (TEM)

1 Introduction

Stick–slip friction is a common phenomenon during the sliding process, which means the contact interface exhibited stick and slip alternately [1, 2]. The occurrence of stick–slip friction would increase the instability and reduce the tribological performance [3, 4]. And there are studies on stick–slip behavior at micro and atomic scales for the materials of amorphous structure [5], oriented crystalline structures like graphene [6] and graphite [7]. Socoliuc et al. [8] observed the existence of smooth sliding with no stick–slip when the load was sufficiently low, which corresponded to extremely low energy dissipation. Wu et al. [9] minimized the stick–slip friction by surface texturing. Peng et al. [10] analyzed the sliding velocity and load effects, which affected the stick–slip friction of 2D material by contact quality and contact area. In those

studies, the stick–slip friction was mainly affected by contact area and the nanostructure in the sliding process. However, the dynamic transition of frictional contact interface during the stick and slip process is still a black box.

For now, the transmission electron microscope (TEM) is an important equipment to *in-situ* observe the nanostructure at atomic scale [11, 12]. It allows us to characterize the sliding interface in the high vacuum environment at micro/nano scales, which can eliminate the external environmental effects and analyze the material transition mechanism at nanoscale [13, 14]. Merkle et al. [15] *in-situ* observed the bonding and structural behavior of the tungsten probe sliding against the diamond-like carbon film in TEM, and suggest that the tribolayers formed with sp^2 bonding increased and graphitization was due to local mechanical excitation at the sliding interface.

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Zhou et al. [16] performed *in-situ* force measurements by a TEM–AFM piezo-driven technique and observed deformation of an individual carbon fiber. Casillas et al. [17] directly *in-situ* observed the atomic sliding of a silicon probe against graphite and molybdenum disulfide, and demonstrated that single layer transfer was the origin of excellent lubricity. However, the *in-situ* observation of dynamic effects of stick–slip friction has not been studied before, which is meaningful to analyze the mechanism of stick–slip character.

Carbon film is a common tribological material [18]. There are already studies reported low or ultra-low friction coefficient due to structural change of the carbonaceous coatings led to graphitization of topmost surface by experimental [19–21] or simulations [22, 23]. Those reported studies implied the effect of graphitization at the topmost surface leading to low friction coefficient. Recent years, the graphene embedded nanocrystallited carbon films exhibited outstanding mechanical behaviors [24, 25] and frictional behaviors [26]. For the sp^2 nanocrystallite embedded carbon film prepared by electron cyclotron resonance (ECR) plasma sputtering system [27], the self-lubrication of sp^2 bonds can reduce the friction coefficient [28], and the sp^3 bonds can enhance the hardness and reduce the wear [29]. However, the carbon film exhibited different extent of stick–slip friction at microscale with nanoscratch test, and the mechanism of origin is still unclear. Therefore, in this paper, sp^2 nanocrystallited carbon films with different shear strengths were prepared by different irradiation particles and energies, the origin of stick–slip behavior of sp^2 nanocrystallited carbon films were studied with *in-situ* TEM friction tests. And the stick–slip behaviors were tested and the mechanisms was verified with the *ex-situ* friction tests.

2 Experimental

2.1 Preparation of sp^2 nanocrystallited carbon film

The sp^2 nanocrystallited carbon films were prepared with ECR plasma sputtering system. Through adjusting the mirror-confined and divergent magnetic fields, and applying positive and negative substrate bias,

different sputtering particles and energies during film deposition process were controlled. For the *in-situ* TEM tests, pure Si wedge with plateau width of 150 nm was used, which was purchased and specially for *in-situ* TEM tests, and for the *ex-situ* tests, p-type Si <100> (thickness, 500 μm ; size, 20 mm $\times$ 20 mm) was used as substrate, which was cleaned in acetone and ethanol bath successively by ultrasonic waves. For the deposition processes of all the films, the chamber was first pumped to a background pressure of 8.0×10^{-5} Pa with mechanical and molecular pumps, and argon was inflated to keep the working pressure with 4×10^{-2} Pa. Then the argon gas was charged with 2.45 GHz microwave at the ECR point where magnetic field was 875 G. The sputtered carbon atoms dropped into plasma by applying bias voltage of -500 V on cylindrical glassy carbon target. The deposition rate was hardly affected by bias voltage but affected by irradiation particles from the results of former experiments. To attract the electrons for electron irradiation [30], mirror-confined magnetic field was used and positive biases of +0, +20, +50, and +80 V were applied on the substrate to prepare carbon film (e-irradiated film for short), the deposition time was 40 min for the film thickness of about 100 nm. To attract the ions for ion irradiation [29], divergent magnetic field was used, and negative biases of -0 , -20 , -50 , and -80 V were applied on the substrate to prepare carbon film (i-irradiated film for short), the deposition time was 30 min for the film thickness of about 100 nm.

2.2 Characterization of sp^2 nanocrystallited carbon films

High-resolution transmission electron microscopy (HRTEM) was used to observe the nanostructures, and electron energy-loss spectroscopy (EELS) was used to analyze the hybridization of the film. TEM specimens for plan view observation were prepared by slightly scratching the film surface with a diamond pencil and transferring the films onto a copper microgrid. Then, the edges of the flakes produced by scratching were observed by using a double spherical aberration correction transmission electron microscope (TEM; ThermoFisher, Titan3 Themis G2, USA) with electron accelerating voltage of 80 kV. The EELS

signal was acquired in TEM mode with exposure time of 0.8 s overlapped with 5 frames for the carbon K edge. The core-loss spectra of carbon were obtained for the analysis of sp^2 and sp^3 hybridization and the low-loss spectra were used for the analysis of carbon atom density. Because the plasmon tail, lower energy core edges, multiple scattering, and instrument noise, the spectra were subtracted by a power-law background fit [31], which also executed a dark correction to remove the effect of electrons collection from the camera. The nanocrystallite structures of the carbon films were analyzed by Raman spectra (HORIBA, HR-Resolution) obtained with a laser wavelength of 532 nm. The laser spot size was focused to $2\ \mu\text{m}$ using a $100\times$ objective, and the laser power was kept at 0.1 mW to avoid sample surface heating. The Raman spectra between $1,100$ and $2,000\ \text{cm}^{-1}$ were acquired and analyzed. The surface morphology of the carbon films was measured by atomic force microscope (AFM, Bruker, USA) under tapping mode. Silicon tip with curvature radius of $2\ \text{nm}$ was used, and the images were obtained with scan size of $1\ \mu\text{m} \times 1\ \mu\text{m}$, scan frequency of $0.75\ \text{Hz}$, and loading force of $2\text{--}4\ \mu\text{N}$. The mechanical properties of the carbon films were tested using a nanoindenter (TI950, Bruker, USA). The Berkovich tip has a total included angle of 142.2° with tip radius about $100\ \text{nm}$. After the system calibration, the elastic modulus and hardness of the carbon films were calculated with the load-displacement curves under indentation load of $500\ \mu\text{N}$, and all the curves were confirmed by three indentation tests under the same conditions. The surface adhesion was tested by a silicon tip contact with the film surface. The force displacement curves were obtained during the approaching and retraction processes to calculate the adhesive force. The tip curvature radius was $4\ \text{nm}$, the cantilever stiffness of the tip was $0.04\ \text{N/m}$, and the loading force was $10\ \text{nN}$.

2.3 In-situ TEM nanofriction test

The *in-situ* nanofriction properties of the sp^2 nanocrystallized carbon films were tested using a picoindenter (PI95, Bruker, USA) in the HRTEM (ThermoFisher, Titan3 Themis G2, USA) with electron

accelerating voltage of $80\ \text{kV}$. Electron irradiated sp^2 nanocrystallized carbon film with substrate bias of $+20\ \text{V}$ and ion irradiated one with bias of $-20\ \text{V}$ were chosen for the *in-situ* TEM nanofriction tests due to the obvious difference of shear strength of the two carbon films. The films for *in-situ* tests were deposited on the silicon wedge substrate with plateau width of $150\ \text{nm}$, and then the film is thin enough for the transmission of electrons without any further thinning process to induce the surface damage. The schematic and apparatus for the *in-situ* TEM nanofriction test are shown in Fig. 1. The film on silicon wedge substrate can be directly mounted on the holder for nanofriction test and TEM observation without any surface damage. The *in-situ* tests were performed with a cube corner tip (curvature radius of $40\ \text{nm}$) indenting and sliding against the film surface. 2D MEMS transducer control the normal and the lateral forces and displacements. The stiffness of the transducer in the normal direction is $220.8\ \text{N/m}$, and in the lateral direction is $145.1\ \text{N/m}$. The force resolutions for normal and lateral directions are 4 and $20\ \text{nN}$, respectively. The nanofriction tests were performed in load control mode and the applied loads were 10 , 20 , and $40\ \mu\text{N}$. The sliding distance was set as $200\ \text{nm}$, and the sliding time was $15\ \text{s}$.

Fig. 1 (a) Schematic and (b) sample holder of *in-situ* TEM nanofriction test.

2.4 Ex-situ nanofriction test

The *ex-situ* nanofriction properties of the sp^2 nanocrystallized carbon films were tested using a triboindenter (TI950, Bruker, USA). The Berkovich tip with nominal tip radius of 100 nm was used to slide against the film surface. Two types of loading mode were used with constant loads of 200, 500, 1,000, 1,500 μN and ramping load of 0–2,000 μN . During the nanofriction tests, 2D transducer was used, which enabled to measure the lateral force during the sliding process. The load resolutions for normal and lateral directions are 1 and 3 μN , respectively. The sliding distance was set as 10 μm , and the sliding time was 15 s. After the sliding process, the wear depth was acquired by scanning the section profiles of the scratch track with the Berkovich tip. The images were obtained with scan size of 15 $\mu\text{m} \times 15 \mu\text{m}$ to cover the whole sliding distance, and the loading force was 2 μN . Then, the wear depth was obtained by made sectional lines across the wear tracks. In order to increase the reproducibility and accuracy of the measurements, we performed the double check measurement.

3 Results and discussions

3.1 Two kinds of sp^2 nanocrystallite structures

The nanostructure of the two representative films

prepared for *in-situ* TEM tests was observed, as shown in Fig. 2. The nanocrystallites can be found from the HRTEM images, which exhibit layer structure. All the insets show two white light spots, indicating the nanocrystallites in carbon films. The core-loss EELS spectra are shown in the lower-right corner. The π^* peak around 285 eV can reflect the presence of sp^2 bond carbon atom, and the shape of σ^* peak around 292 eV can reflect the nanostructure. The e-irradiated carbon film shows a sharp peak around 292 eV, which means the sp^2 nanocrystallites are larger than i-irradiated carbon film, and it also can be seen from the images. The ratio of A_{π^*} to $A_{\pi^*+\sigma^*}$ had been calculated to qualitatively compare the sp^2 percentage [32]. The data range of π^* peak and $(\pi^* + \sigma^*)$ peak took a 5 eV window (283–288 eV) and a 20 eV window (283–303 eV) in carbon K-edge, respectively. The results exhibited that the i-irradiated carbon film had the smaller ratio of area (π^*) to area $(\pi^* + \sigma^*)$, which meant the ion irradiated ones had lower sp^2 percentage.

The low energy loss spectra obtained with EELS showed the plasmon peaks, which were generated by the inelastic scattering of valence electrons. As shown in Fig. 3(a), the energy is proportional to the square root of the electron density, which referred to density of the carbon films [31, 33]. The central line of ion irradiated carbon films was closer to the right, which means the density was higher than electron irradiated

Fig. 2 HRTEM images for the carbon films deposited with +20 and –20 V, respectively. The insets in the images show the diffraction patterns, and the lower-right shows the core-loss EELS spectra with π^* and σ^* peaks. The ratio of area (π^*), A_{π^*} to area ($\pi^* + \sigma^*$), $A_{\pi^*+\sigma^*}$ was calculated.

Fig. 3 Characterizations for two kinds of representative carbon films for *in-situ* TEM nanofriction tests. (a) Low energy loss spectra of the carbon films; (b) Raman spectra of the carbon films; (c) the adhesive force and surface roughness of the carbon films; and (d) the elastic modulus and hardness of the carbon films.

ones. The Raman spectra of the films are shown in Fig. 3(b). Comparing with a wide range peak of the i-irradiated film, the e-irradiated carbon film exhibited sharp D peak and G peak obviously, which meant the sp^2 bonds formed crystalline cluster more than ion irradiated ones [34]. And the ratio of intensity of D peak around $1,340\text{ cm}^{-1}$ and G peak around $1,590\text{ cm}^{-1}$ can be obtained by peak fitting of Raman spectrum, the Lorentzian peak for D peak and the Breit-Fana-Wagner (BFW) peak for G peak [35]. The ratios of D peak to G peak (I_D/I_G) were 1.15 for electron irradiated ones and 0.37 for i-irradiated ones, which meant the e-irradiated carbon film had larger nanocrystallite size. The adhesive force together with the surface roughness of the two kinds of carbon films are shown in Fig. 3(c), since the load for adhesive test was small to generate elastic deformation, the i-irradiated carbon film showed smooth surface with roughness of 0.1 nm, and larger adhesive force of 7.9 nN, while for the e-irradiated film with rougher surface with roughness of 7.1 nm, the adhesive force

decreased to about 4.1 nN due to small contact area. Figure 3(d) exhibits the load–displacement curves of the films tested with the nanoindentation method. In this study, the mechanical behaviors were attained with thicker films to avoid the substrate effect. With the same load, the e-irradiated sp^2 nanocrystallited carbon film generated much deeper indentation depth, which means the ion irradiated ones had higher elastic modulus, hardness, and shear strength than electron irradiated ones.

3.2 *In-situ* TEM nanofriction properties

The *in-situ* nanofriction tests were performed to investigate the origin of stick–slip friction. And the *in-situ* variations of friction coefficient together with the contact status are shown in Fig. 4. In Fig. 4(a), the e-irradiated carbon film showed severe stick–slip friction. The degree of stick increased with the increasing of load, and the tip was fully adhered when the load was 40 μN . The video of dynamic sliding process under the load of 10 μN was shown

Fig. 4 *In-situ* nanofriction test results. (a, b) Friction coefficient curves of the films prepared with +20 and –20 V under the load of 10, 20, and 40 μ N. The insetted Figs. I–VIII show the *in-situ* nanofriction states of the marked position in (a) and (b).

in Video S1 in the Electronic Supplementary Material (ESM), showing that the contact between the tip and the film surface firstly strengthened with a gradually increased stick area, and bended the nanocrystallited film with the trend of sliding, when the shear stress exceeded the adhesive strength, the tip suddenly slipped over with a much smaller contact area. Then the tip went into another stick–slip stage. Four different stick–slip stages were marked with I–IV in Fig. 4, and the corresponding contact status observed with TEM images were shown with insetted Figs. I–IV. In the insetted Fig. I, the tip was just contact with the surface without applying load. In the insetted Fig. II, when the stick increased to a critical stage, the contact area was large. In the insetted Fig. III, when the slip happened, the contact area was obviously decreased, which meant the unstable sliding process of the electron irradiated ones. In the insetted Fig. IV, after the nanofriction test, there was abrasive wear particle showed on the surface, which generated by the adhesion between the tip and the surface, and it can

be verified with the Video S1 in the ESM. In Fig. 4(b), the i-irradiated carbon film also showed that the contact strength increased at first, and then the tip slid against the film with slight vibration and smoother sliding process. The video of dynamic sliding process under the load of 10 μ N was shown in the Video S2 in the ESM, after sliding process, a long wear track was generated with the tip ploughing against the film. The different states of the friction curve had been marked in the insetted Figs. V–VIII. It can be found from the insetted Figs. VI and VII that the contact area of ion irradiated ones was almost the same during the stick and the slip process, after the test, ploughing track can be observed in the insetted Fig. VIII. When the load was 20 μ N, the stick–slip friction got severed due to the increasing of load, the videos of dynamic sliding processes of electron and ion irradiated carbon films were shown in the Videos S3 and S4 in the ESM, respectively. The variations of normal force, lateral force, and lateral displacement with time were recorded during the *in-situ* tests, as

shown in Fig. S1 in the ESM. The normal force fluctuated at the slip stage when the tip sliding against the e-irradiated carbon film under the load of 10 μN , while the normal load barely changed for the other cases, as shown in Figs. S1(b)–S1(f) in the ESM. In the experiments, the tip was driven with an effective spring constant, which combines the stiffness in the normal and lateral directions. The stiffness in the normal direction affected the moving path through restrain the energy accumulation in the cantilever [36, 37]. In this study, the stiffness in the normal direction is much larger than the lateral stiffness, which means the tip shift in normal direction is small, and tip moves along the lateral driving direction.

The friction coefficient curves of two different carbon films with the corresponding variations of contact area and shear stress under the loads of 10, 20,

and 40 μN were calculated and shown in Fig. 5, and the variation of friction coefficient from stick stage to slip stage had been labeled. From the *in-situ* images, the contact depth (h_c) and contact width (w) can be obtained directly, which can be used to calculate the equivalent radius (R_{eq}) and contact area (A_c) by the following functions since the residual scratch angle was larger than 150° [38]:

$$R_{eq} = \frac{1}{2} \left(h_c + \frac{w^2}{4h_c} \right) \quad (1)$$

$$A_c = 2\pi h_c \cdot R_{eq} \quad (2)$$

And the shear stress at the contact area can be obtained by dividing contact area into friction force. In Fig. 5(a), the electron irradiated carbon film exhibited severe stick–slip friction with the load of 10 μN . The

Fig. 5 Friction coefficient curves of two different carbon films with the corresponding variations of contact area and shear stress under the load of 10, 20, and 40 μN , respectively.

shear stress increased gradually at the stick stage and decreased at the slip stage, which caused the unstable sliding process and severe stick–slip friction, the friction coefficient changed from 1.04 at stick stage to 0.57 at slip stage. In Fig. 5(b), the i-irradiated carbon film exhibited mild stick–slip friction with the load of 10 μN . The contact area changed a little, while the shear stress increased at the stick stage and decreased at the slip stage. The largest variation of friction coefficient was from 0.70 to 0.42 when the stick–slip friction happened. In Figs. 5(c) and 5(d), the two carbon films both exhibited stick–slip friction with the load of 20 μN . For the e-irradiated carbon film, the contact area and shear force increased at the stick stage and decreased at the slip stage, and the friction coefficient changed from 1.12 to 0.72 when the stick–slip friction happened. For the i-irradiated carbon film, the contact area and shear force increased at the stick stage, and then the shear force fluctuated due to the variation of contact area at the slip stage, and the friction coefficient did not change a lot. In Figs. 5(e) and 5(f), when the load increased to 40 μN , the contact area and shear stress increased and tip was totally adhered without any slip within the settled sliding time, which meant the tip was still at the shear strength stage and did not reach the critical value.

With the *in-situ* TEM nanofriction tests in high vacuum, the external environmental effects were eliminated, the tip was driven by a cantilever to slide with the surface of sp^2 nanocrystallited carbon films, which is similar with the AFM friction. In the atomic scale, the Prandtl–Tomlinson (P–T) model dominate the understanding of stick–slip [39–41]. In this research, a minimum force to the slider for the “pretensioning” of the spring between point mass and slider was also needed to overcome potential barriers, as the first friction force increasing stage in this manuscript. However, when sliding begins, considering the rough contact and the tip–sample adhesion, the stick–slip cannot be explained with the P–T model. First, the realistic microscale contact was not periodical, and the rough surface asperities may sustain plastic deformation; second, the tip–surface adhesion in the normal direction cannot be ignored, which can affect tip moving from one potential minimum to another. The large-scale friction coefficient depended on the

system parameters like surface roughness, separation, and direction can be originated from the nanoscale dislocation plasticity [42]. Therefore, the intrinsic factors affect the sliding process through the transition of contact area and film deformation. The nanostructures of sp^2 nanocrystallited carbon films were mainly defined by the irradiation particles, which caused the differences of film densities, surface roughness, elastic modulus, hardness, and shear strength, then finally affect the stick–slip friction. According to the von Mises yield criteria [43], the shear yield strength of adhesion strength was about 0.57 times hardness of the carbon films, which were 2.5 GPa for electron irradiated carbon film (S_e) and 13.1 GPa for ion irradiated carbon film (S_i), respectively. For e-irradiated carbon film, the shear stress at the stick stage increased to 4.2 GPa and reached S_e with the load of 10 μN . Adhesion between the tip and film surface asperity happened, resulted in a severe stick–slip friction. While for the i-irradiated carbon film, the shear stress was 7.6 GPa at most and much lower than S_i with the load of 10 μN . Ploughing between the tip and film surface happened with a more stable sliding process. To evaluate the contact mode and contact stress effect, the contact pressure at the initial stage and the contact stress during the sliding process were calculated according to the normal load and the contact area, which were added in Fig. S2 in the ESM. At the initial stage, the contact pressures were all smaller than the hardness of sp^2 nanocrystallited carbon films, meaning the tip elastically contacted with the sample. For the e-irradiated carbon film tested with load of 10 μN , plastic contact occurred during the sliding process because the contact depth is swallow and the surface asperities blocked the tip. For the other cases, the contact area gradually increased with the sliding time, which may result from the enhancement of adhesive strength between the contact surfaces [6]. Therefore, the contact stresses gradually decreased and were all smaller than the hardness during the sliding processes. As a result, the effects of contact stress and tip–surface adhesion in the normal direction were ignored, and the different stick–slip characters were ascribed to the shear stress and the film deformation due to different surface property and nanostructure of sp^2 nanocrystallited carbon films.

Figure 6 exhibited two different plastic deformation type of electron and ion irradiated carbon films. For e-irradiated carbon film with lower density, higher surface roughness, and lower hardness, the tip was easier to stick on the film surface due to the adhesion with a contact strengthening process, the contact area grew until the static force reached the critical shear value [44–46]. During this period, the area behind the probe showed breakage and the breakage broadened gradually, as shown in Figs. 6(a) and 6(b). Then the energy stored in the stick process dissipated [47], resulting in a large area of plastic deformation on the contact area, as shown in Fig. 6(c). For i-irradiated carbon film shown in Figs. 6(e)–6(g), the contact strengthened at first, and when the shear strength is high enough to break the stiction, the tip ploughed on the film surface. Because of the high film density, lower surface roughness, and higher hardness, the contact area was changed small, and the carbon film exhibited a smooth and stable sliding process. Figures 6(d)

and 6(h) exhibited the deformations after the *in-situ* nanofriction tests. For the e-irradiated carbon film, the large areas of plastic deformation can be found in the carbon films due to the shear stress arrived S_e . The largest depth of adhesion deformation was 55.4 nm with the load of 10 μN , which was much deeper than the contact depth of 18.6 nm at the stick stage. It meant the severe stick–slip friction was due to the adhesion. For the i-irradiated carbon film, the plastic deformation type was ploughing due to the shear stress was lower than S_i . The largest depth of ploughing was 10.5 nm with the load of 10 μN , which was shallower than the contact depth of 14.7 nm at the stick stage. When the load was 20 μN , the deformations of films were nearly the same with those at the load of 10 μN , as shown in Fig. S3 in the ESM. The surface deformation of the e-irradiated carbon film leads to larger adhesive force. Therefore, combined with the larger shear stress and surface deformation effects, different types of stick–slip

Fig. 6 (a–d) Large area adhesion of plastic deformation caused by stick–slip friction of e-irradiated sp^2 nanocrystallited carbon film and (e–h) ploughing of plastic deformation with a stable sliding process of i-irradiated sp^2 nanocrystallited carbon film.

phenomenon happened for the realistic nanofriction of sp^2 nanocrystallited carbon films. The origins of stick and slip varied with shear stress and film deformation, which was affected by the film density, and surface roughness and hardness. Higher film density, lower surface roughness, and higher hardness promise the stable of contact area with ploughing of plastic deformation.

3.3 sp^2 nanocrystallited carbon films with different irradiation energies

sp^2 nanocrystallited carbon films with different electron and ion irradiation energies were prepared to investigate the *ex-situ* frictional application. The values of I_D/I_G of sp^2 nanocrystallited carbon films with different irradiation energies are shown in Fig. 7(a), for e-irradiated carbon films, the value of I_D/I_G was high and at the range of 0.55–1.66. By contrast, the i-irradiated carbon films were at the range of 0.28–0.44, which means electron irradiated ones had the larger size of sp^2 nanocrystallites than the ion irradiated ones. The original Raman spectra are shown in Fig. S4 in the ESM. The average surface roughness (R_a) of the sp^2 nanocrystallited carbon films were measured and shown in Fig. 7(a). The surface with ion irradiation was much smoother than the e-irradiated one with large domes. For the i-irradiated carbon films with the ion excitation and etching effect [28], the surfaces were flat with small asperities, and values were all around 0.1 nm with different irradiation energies. While for the e-irradiated carbon films, since the temperature during film deposition was much higher [48], the roughness

changed a lot with different irradiation energies, the maximum roughness of 7.1 nm appeared with substrate bias of +20 V, and then the roughness decreased to 2.2 nm with the increasing of electron irradiation energy increased to +80 V. The elastic modulus and hardness of the sp^2 nanocrystallited carbon films also showed great difference for the electron and ion irradiated films due to the differences of nanostructure (shown in Fig. 7(b)). The sp^2 nanocrystallited carbon films prepared with ion irradiation exhibited elastic modulus of ~180 GPa, and the hardness slightly increased from 21.8 to 23.9 GPa with the irradiation energy increased. For the films prepared with electron irradiation, the hardness decreased from 15 to ~4.4 GPa when the electron irradiation started to work at +20 V.

As discussed above, the growth of sp^2 nanocrystallites in the e- and i-irradiated films were quite different. With 0 V applied, the mirror-confined and divergence magnetic field pattern were adopted to prepare the e- and i-irradiated carbon films, respectively. The plasma sheath before the substrate attracted ions accelerated to the surface, and the different nanostructure mainly due to the pattern of magnetic field. The mirror-confined magnetic field used for e-irradiation formed the ECR plane around the substrate, which would enhance the sp^2 bond forming. With (−80)–(−20) V applied, the ions accelerated to the surface, induced the growth of carbon film by ion excitation effect or ion etching effect, and the top-most carbon atoms were excited or moved to form the sp^2 bond [29]. Furthermore, the ions can get high kinetic energy during the acceleration process due to its own

Fig. 7 (a) I_D/I_G and average surface roughness R_a of the sp^2 nanocrystallited carbon films with different substrate biases and (b) elastic modulus and hardness of the sp^2 nanocrystallited carbon films with different substrate biases.

quality, the ion irradiated ones can get smoother surface and higher film density than electron irradiated ones. Because the different forming type of sp^2 nanocrystallite, the i-irradiated carbon films got smaller nanocrystallite size and formed much cross-linking structure, which enhances the elastic modulus and hardness. With (+20)–(+80) V applied, the electrons were accelerated to the surface, and induced the hybridization changed from sp^3 to sp^2 due to the low energy electrons exchanged energy with valence electrons of carbon atoms by inelastic scattering [49]. The e-irradiated carbon films had larger nanocrystallite size, lower film density, higher surface roughness, lower elastic modulus, and hardness.

3.4 Ex-situ nanofriction properties

For further study the stick–slip friction of sp^2 nanocrystallited carbon films and the *ex-situ* nanofriction tests of the films with different irradiation energies were tested with a diamond tip (curvature radius of 100 nm) sliding against the films at

atmosphere environment, and the results are shown in Fig. 8. The *ex-situ* friction of sp^2 nanocrystallited carbon films exhibited similar sliding behavior with the *in-situ* results. Figure 8(a) exhibit the friction coefficient curves of the films prepared with +20 and –20 V under the load of 500 μN . The i-irradiated carbon films exhibited smooth sliding process with average friction coefficient of 0.12, while friction curve of the e-irradiated film exhibited stick–slip friction with average friction coefficient of 0.18. The friction curves of sp^2 nanocrystallited carbon films with different irradiation energies under the constant load of 500 μN and ramping load of 0–2,000 μN are shown in Fig. S5 in the ESM, the e-irradiated carbon films exhibited unstable sliding process while the ion irradiated ones showed more stable sliding process. Figure 8(b) summarize the average friction coefficient of the sp^2 nanocrystallited carbon films, under the loads of 200, 500, 1,000, and 1,500 μN , the friction coefficients of i-irradiated carbon films were much lower than e-irradiated ones. The worn

Fig. 8 *Ex-situ* nanofriction test results. (a) Two typical friction coefficient curves of the films prepared with +20 and –20 V under the load of 500 μN ; (b) summarized friction coefficient for the sp^2 nanocrystallited carbon films with different loads; (c) two typical worn surfaces of the films prepared with +20 and –20 V under the loads of 500 and 1,000 μN ; and (d) summarized scratch depth for the sp^2 nanocrystallited carbon films with different loads.

surfaces with scratch tracks are shown in Fig. 8(c), and the tracks were more obvious for the e-irradiated films than those on the ion irradiated ones under same load. The scratch depths can be obtained by a cross-sectional plane, which are summarized in Fig. 8(d), and the scratch depths of i-irradiated carbon films were much shallow than the e-irradiated ones under same load. The *ex-situ* friction tests showed the same sliding behavior with the *in-situ* tests.

With the stable sliding process, i-irradiated carbon films had lower friction coefficients and shallower scratch depths. It had been studied that stick–slip instability can be affected by the external factors like sliding velocity, normal load, and environment [50]. Here, we kept these factors same to focused on the basic effects by internal factors as studied with the *in-situ* tests. Due to the lower film densities, higher surface roughness, and lower hardness of e-irradiated carbon films, contact area was larger than the ion irradiated ones during the sliding process. And the shear stress can be calculated by dividing friction force by contact area. For e-irradiated carbon films, the shear stress was about 0.8–1.2 GPa, which differed about 1.5 GPa and closed to S_e (about 1.5–3.1 GPa). It meant that the severe stick–slip friction happened was due to the adhesion, and this was exactly the reason why the friction coefficient of electron carbon films was almost same. For ion irradiated ones, the shear stress was about 1.7–4.2 GPa, which differed about 10.5 GPa and far less than S_i (about 13.1–13.6 GPa). It meant that the plastic deformation was due to the ploughing. At the ploughing effect, the friction coefficient and scratch depth of i-irradiated carbon films increased gradually with the load increased and had a smooth and stable sliding process. Therefore, the *ex-situ* nanofriction tests verified that the origin of stick–slip friction was mainly due to the shear stress variation and film deformation, which was affected by the film density, and surface roughness and hardness.

4 Conclusions

Carbon films with two different kinds of sp^2 nanocrystallited structure were investigated to study the

stick–slip friction with the *in-situ* TEM and *ex-situ* tests. The ECR plasma sputtering system was used to prepare the carbon films with different sp^2 nanocrystallite size, film density, surface roughness, and hardness. *In-situ* TEM observation and nanofriction tests revealed that origin of stick and slip varied with shear stress and film deformation, which was affected by the film density, surface roughness, and hardness. Higher carbon density, lower surface roughness, and higher hardness promise the stable of contact area with ploughing of plastic deformation, leading to a smooth sliding process. While for the film with lower film density, higher surface roughness, and lower hardness, the shear stress first gradually increased with the contact strengthened to the critical value of adhesion, the contact changed from stick stage to slip stage causing a large area adhesion of plastic deformation. *Ex-situ* nanofriction tests on a series of sp^2 nanocrystallited carbon films with different irradiation energies showed the same scratch behavior with the *in-situ* results. For the films with smooth sliding process exhibited lower friction coefficient of 0.08, and shallower scratch depth of 0.26 nm, and the friction coefficient increased with load due to the ploughing of plastic deformation. For the films with unstable stick–slip friction showed higher friction coefficient of 0.18 and deeper scratch depth of 46 nm was obtained due to adhesion effect. This study first clarified the mechanism of stick–slip friction with the *in-situ* TEM observation, which plays an important role for the micro and nano application of sp^2 nanocrystallited carbon films.

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