Ion energy-induced nanoclustering structure in a-C:H film for achieving robust superlubricity in vacuum

Qingyuan YU, Xinchun CHEN*, Chenhui ZHANG*, Chenxi ZHANG, Wenli DENG, Yinhui WANG, Jianxun XU, Wei QI

State Key Laboratory of Tribology, Tsinghua University, Beijing 100084, China

Received: 09 July 2021 / Revised: 17 August 2021 / Accepted: 20 September 2021

© The author(s) 2021.

Abstract: Hydrogenated amorphous carbon (a-C:H) films are capable of providing excellent superlubricating properties, which have great potential serving as self-lubricating protective layer for mechanical systems in extreme working conditions. However, it is still a huge challenge to develop a-C:H films capable of achieving robust superlubricity state in vacuum. The main obstacle derives from the lack of knowledge on the influencing mechanism of deposition parameters on the films bonding structure and its relation to their self-lubrication performance. Aiming at finding the optimized deposition energy and revealing its influencing mechanism on superlubricity, a series of highly-hydrogenated a-C:H films were synthesized with appropriate ion energy, and systematic tribological experiments and structural characterization were conducted. The results highlight the pivotal role of ion energy on film composition, nanoclustering structure, and bonding state, which determine mechanical properties of highly-hydrogenated a-C:H films and surface passivation ability and hence their superlubricity performance in vacuum. The optimized superlubricity performance with the lowest friction coefficient of 0.006 coupled with the lowest wear rate emerges when the carbon ion energy is just beyond the penetration threshold of subplantation. The combined growth process of surface chemisorption and subsurface implantation is the key for a-C:H films to acquire stiff nanoclustering network and high volume of hydrogen incorporation, which enables a robust near-frictionless sliding surface. These findings can provide a guidance towards a more effective manipulation of self-lubricating a-C:H films for space application.

Keywords: hydrogenated amorphous carbon (a-C:H); superlubricity; ion energy; nanoclustering; bonding structure; mechanical properties

1 Introduction

Diamond-like carbon (DLC) films are well known for their superior mechanical properties, chemical inertness, and especially excellent self-lubricating performance [1, 2], and they have been widely accepted as one of the most promising self-lubricating protective layers in mechanical systems [3–19]. Recently, it was reported that sufficient hydrogen incorporation can make DLC films capable of achieving near-frictionless sliding state with an extremely low friction coefficient (below 0.01) and negligible wear when rubbed in dry inert atmosphere such as nitrogen, carbon dioxide, and argon

[3, 20–33]. Research showed that the mechanism of superlubricity achieved with a-C:H films was multifaceted and interrelated [24, 25], while the pivotal role of hydrogen was highly emphasized [24, 25, 27, 34, 35]. It is widely accepted that the hydrogen contained in the film can passivate the surface with C–H terminations during sliding contact, preventing the establishment of sliding interfaces with covalent bridging, which could restrain adhesion effects to an extremely low state, and hence lead to low friction [27].

The superlubricity behavior of a-C:H films has tremendous potential applications for reducing energy consumption in future advanced mechanical systems,

* Corresponding authors: Xinchun CHEN, E-mail: chenxc1213@mail.tsinghua.edu.cn; Chenhui ZHANG, E-mail: chzhang@tsinghua.edu.cn

especially for aerospace applications [36–38]. However, even though a-C:H films are capable of achieving superlubricity in vacuum [29, 39], their wear rate is very high [38, 40] (typically more than $1 \times 10^{-5} \text{ mm}^3 \cdot \text{N}^{-1} \cdot \text{m}^{-1}$ [41, 42], about two orders of magnitude higher than that in air [36]), which is the main obstacle for their applications in space [38, 43]. The mechanism of high wear rate of a-C:H in vacuum originates from the higher chance of hydrogen detachment, indicating that increasing hydrogen proportion is probably the most straightforward and effective way to combat this defect. For example, experimental studies showed that the lifetime of a-C:H was elongated from 40 cycles to more than 500 cycles when hydrogen content increased from 34% to 40% when tribo-tested in vacuum [43].

However, the influence of hydrogen in the film property is multifaceted, which is not always positive. Some experimental studies show that the friction coefficient exhibits an increasing tendency when the hydrogen content exceeds a threshold [44, 45], which has not been detailly illustrated. Investigations show that overhigh hydrogen content can also deteriorate the superlubricious life time of a-C:H, which may be closely interrelated with the stiffness of bonding network [46]. Meanwhile, the upper limit and optimized hydrogen content for space application and the corresponding structural evolution still need systematic studies. The film growth mode and its influencing mechanism on superlubricity are still not well understood, which poses uncertainties for their applications.

In addition, the bonding state of carbon skeleton is also important for the realization of superlubricity. Both experimental and simulation results suggest that the tribo-induced rehybridization of carbon network from sp^3 to sp^2 and their reorientation towards layer-like structure may also account for the formation of easy-shearing interfaces, which contributes to the self-lubricating behavior [47–59]. However, for traditional a-C:H synthesized with hydrogen and alkanes, the sp^2 ratio decreases with hydrogen content [60], which makes it hard to investigate the influences of bonding hybridization and surface passivation independently. To fill in this blank, it is advisable to synthesize a-C:H film from gas sources with sufficient supply of sp^2 carbon structure such as aromatic clusters. Ion beam deposition (IBD) is one of the most powerful synthesis

methods for developing superlubricious a-C:H films owing to its advantage in accurately controlling ion energy as well as its diversified choices of gas sources, which could enable the achievement of precisely-tailored bonding structure and elemental composition [44, 48, 61, 62].

Aiming at optimizing the self-lubricating and anti-wear performance of a-C:H films in vacuum as well as revealing the influencing mechanism of deposition parameters on the tribological properties of a-C:H films, we synthesized a series of a-C:H films from toluene gas source with controlled parameters in an IBD system. The self-lubricating performance was examined in vacuum to explore the optimal ion energy for growing a tough film by adjusting the bias voltage applied to the substrates. Systematic characterizations were conducted on the evolution of nanoclustering structure, bonding state, and nanomechanical properties as a function of bias voltage. The results indicate that the self-lubricating ability of a-C:H films is closely related to the nanoclustering structure deriving from the growth mechanisms governed by the deposition ion energy. These interesting findings can provide new knowledge on the structural manipulation of superlubricious a-C:H films prepared for engineering applications in aerospace or other extreme environments.

2 Experimental

2.1 Deposition of a-C:H films

This methodology was proposed by Weissmantel et al. [63], and its application for synthesizing superlubricious carbon films was explored by Chen et al. [44, 48, 61, 62]. Bilayered carbon films with different a-C:H top layers were deposited on silicon wafer via IBD method using evaporated toluene and tetramethylsilane (TMS) gas sources. The main part of the deposition system consists of a tantalum filament, a triangular-shaped anode, and a substrate bias voltage assembly. During the deposition process, gas source molecules were ionized by electrons emitted from the filament. Then these ions were accelerated by the electric field between the ion source and sample holder, forming a broad ion beam and bombarding on the negatively-biased samples, which produced a-C:H coatings [62]. Single

crystal silicon substrates were ultrasonically cleaned with acetone. After installation to the sample holder, the vacuum chamber was pumped down to 1.0×10^{-3} Pa, and then heated to 200 °C. Afterwards, the substrate surface was bombarded with Ar⁺ beam for 30 min to remove adsorbed contaminations. A silicon-containing hydrogenated amorphous carbon (a-C:H:Si) with a thickness around 0.25–0.35 µm was first deposited using a mixture of toluene and TMS, serving as a transition layer to enhance bonding strength. Then, a polymer-like carbon (PLC) type of a-C:H films with thickness of around 0.60–1.10 µm were deposited with 25% duty-pulsed bias voltage from 0.20 to 0.50 kV using pure gaseous toluene with a constant pressure of 0.5 Pa.

2.2 Characterization

The friction experiments were conducted by HV-TRB (Anton Paar, Austria) under vacuum. The counterparts of PLC films were SUJ2 steel balls with a diameter of 6 mm, and all the samples were ultrasonically cleaned with acetone before the experiment. The temperature was 25 ± 1 °C, and the vacuum pressure was kept below 0.01 Pa. The normal load was 5 N, yielding a maximum Hertz contact pressure of 1.10 GPa. The sliding mode was reciprocating, with an average sliding speed of 8 mm/s and a sliding stroke of 4 mm. The films were tested for 2,400 cycles or until they were worn out. After friction test, the surface topology of wear tracks was characterized with three-dimensional (3D) white-light interferometer (ZYGO NexView, USA), and the wear rate was calculated from the cross-sectional area of the wear track center. Three independent experiments were conducted for each sample to guarantee reproducibility.

The film thickness was measured from the cross-sectional scanning electron microscope (SEM; Hitachi, SU 8220, Japan) images of samples, and the deposition rate was calculated correspondingly. Energy-dispersive spectroscopy (EDS; Bruker FlatQuad, Germany) scanning was conducted to confirm the boundary of bilayered structures. The surface morphology and roughness were probed by atomic force microscope (AFM; Bruker Dimension ICON, Germany) in tapping mode. An evaluating area of $2.5 \mu\text{m} \times 2.5 \mu\text{m}$ was tested for each sample with a 10-nm-radius silicon tip at a scanning speed of 5 µm/s, and 512×512 z-height data points were acquired from each scanning. The scanning

was repeated three times for calculating the average roughness Ra of each sample. To investigate the nanostructure inside the films, transmission electron microscope (TEM; JEOL 2010F, Japan) characterization was conducted on the thin lamellar nanoflakes with a thickness less than 100 nm acquired by focused ion beam (FIB) slicing from the sample surfaces, and the collected ultrathin edges of film debris scratched by diamond pin. X-ray photoelectron spectroscopy (XPS; PHI Quantera II, Japan) analysis was conducted to acquire bonding information of the a-C:H films. Before acquisition, all the samples were ultrasonically cleaned with acetone and sputtered with low energy Ar⁺ to remove the possible contamination on the surface. Further bonding information of the films was characterized by Raman spectra with 532 nm laser. The hardness, elastic modules, and recovery rate of the a-C:H films were characterized by nanoindentation. All tests were conducted at a constant strain rate of 0.042 s^{-1} . The maximum indentation depth was $10 \pm 2\%$ of the film thickness to avoid interference of substrate and sublayer. Each measurement was repeated five times to guarantee reproducibility.

3 Results

3.1 Superlubricity in vacuum

As shown in Fig. 1(a), the highly hydrogenated a-C:H films deposited under low energy around 0.20 and 0.25 kV exhibited a decreasing friction coefficient from 0.04 to 0.02 during the friction test, and the latter film showed a longer life time during experiment. It is noticeable that when the deposition energy increased to 0.30 kV, the a-C:H films showed an ultra-low friction coefficient below 0.01 during the whole test. The lowest friction coefficient reached 0.006, and it increased slightly during the friction test. However, when the applied bias voltage further increased to 0.35 and 0.40 kV, though the films were still capable of achieving a superlubricity state with the lowest friction coefficients around 0.006–0.008, their life time was significantly shortened, surviving around 600 and 300 cycles, respectively. In comparison, when the deposition energy reached 0.50 kV, the film only lasted for 100 cycles in vacuum with the lowest friction coefficient around 0.01.

Fig. 1 Tribological properties of PLC films in vacuum. (a) Friction curves of a-C:H films with varied deposition bias voltages; (b) average steady-state friction coefficients after the 50-cycle running-in period and wear rates of the film surfaces as a function of bias voltage.

The average friction coefficient at the 50th cycle of three independent experiments and the wear rates of the central region of wear track are displayed in Fig. 1(b) as a function of deposition bias voltage. At 0.20 kV, the wear rate of the film was $3.67 \times 10^{-5} \text{ mm}^3 \cdot \text{N}^{-1} \cdot \text{m}^{-1}$, coupled with a relatively high friction coefficient around 0.04. As the voltage was elevated from 0.20 to 0.30 kV, the wear rates were reduced to $6.57 \times 10^{-6} \text{ mm}^3 \cdot \text{N}^{-1} \cdot \text{m}^{-1}$ at 0.25 kV and $1.21 \times 10^{-6} \text{ mm}^3 \cdot \text{N}^{-1} \cdot \text{m}^{-1}$ at 0.30 kV, which was nearly one magnitude lower than the typical value of DLC films around $1 \times 10^{-5} \text{ mm}^3 \cdot \text{N}^{-1} \cdot \text{m}^{-1}$ in vacuum [36, 38, 64, 65]. Synergistically, the friction coefficient also dropped from 0.04 to an ultra-low value below 0.01, reaching the superlubricity state. It is noticeable that the film deposited at 0.30 kV not only exhibited the most prevailing superlubricity state in vacuum, but also showed a most favorable wear rate. However, when the bias voltage increased to 0.35 kV, though the film can still reach the superlubricity state, the wear rate suddenly increased to $6.72 \times 10^{-5} \text{ mm}^3 \cdot \text{N}^{-1} \cdot \text{m}^{-1}$. The same was true with the film deposited at 0.40 kV that the wear rate further increased to $7.87 \times 10^{-5} \text{ mm}^3 \cdot \text{N}^{-1} \cdot \text{m}^{-1}$ with a short superlubricity state, and the film deposited at 0.50 kV showed the highest wear rate of $1.61 \times 10^{-4} \text{ mm}^3 \cdot \text{N}^{-1} \cdot \text{m}^{-1}$, which was soon worn out without achieving a superlubricity state.

3.2 Nanostructure dependent on ion energy

SEM and EDS characterizations were conducted to acquire the cross-sectional structure of the a-C:H films. As shown in Figs. 2(a) and 2(b), the bilayered carbon films with clear and smooth boundaries were deposited on silicon substrates. The thicknesses of a-C:H:Si transition layers were around 0.25–0.35 μm , and that of the a-C:H self-lubricating layers were around 0.60–1.10 μm . It is noticeable that the highest wear depth of the films deposited at 0.30 kV was below 200 nm according to characterizations, which implies that the superlubricous sliding surfaces were specifically established by the top polymer-like a-C:H layer. Here, the a-C:H:Si sublayer served mainly as a transition layer for enhancing the bonding strength between the a-C:H film and the silicon substrate. Meanwhile, the relatively high hardness of this sublayer provides stress-bearing support for the overall loading capacity of the bilayer structure. The evolution tendency of deposition rate with elevated bias voltage was shown in Fig. 2(c). With the increase of bias voltage, the deposition rate first decreased from 2.81 to 1.88 $\text{nm} \cdot \text{s}^{-1}$. It reached the lowest at 0.30 kV, and then gradually increased to 3.62 $\text{nm} \cdot \text{s}^{-1}$ at 0.5 kV.

The surface nano-morphologies of a-C:H films were probed by AFM, as shown in Fig. 3(a). The scanned regions were $2.5 \mu\text{m} \times 2.5 \mu\text{m}$, and the 3D images were all displayed with a same scale bar in height. The surface average roughness of the films as a function

Fig. 2 Overall cross-sectional structure of the bilayered films and ion energy dependence of deposition rate. (a) SEM image showing the cross-sectional morphology of the film and (b) the corresponding EDS scanning. (c) Deposition rates of a-C:H film in relation to the applied bias voltage.

Fig. 3 Surface morphologies of a-C:H films characterized by AFM. (a) 3D-displayed surface morphologies with a same altitude coordinate; (b–e) topographies of asperities on the a-C:H films (the subtracted asperities were marked in blue), the scale bar is 500 nm in length; and (f) surface roughness as a function of deposition bias voltage.

of deposition bias voltage are shown in Fig. 3(f). It is obvious that the surface roughness decreased with bias voltage, from 2.04 nm at 0.20 kV to 0.38 nm at 0.50 kV. The surface of the film grown at 0.20 kV was composed of disordered protuberances with several nanometers high. These nanostructures gradually disappeared with the elevated bias voltage. Interestingly, as shown in Figs. 3(b)–3(e), these nano-asperities seem to still exist under high deposition energy, but evolved from sphere-like structures to disordered network-like structures. The top 100 largest peaks were subtracted by particle analyzing tools and marked in blue in the inserted figures, and the diameters of these asperities were all around 70 nm. These results imply that the island growth mode based on surface chemical process in low deposition energy [66, 67] may be still valid under the higher applied bias voltage. Meanwhile, the higher ion energy tended to smash and flatten these asperities by the erosions of hills into neighboring hollows due to the enhanced downhill currents at atomic scale, which was predicted by the simulations conducted by Moseler et al. [68].

The nanoclustering structures inside the a-C:H films were characterized by TEM. As mentioned above, two different methods were used for sample preparation. Figures 4(a)–4(c) show the TEM images of a-C:H samples prepared by FIB slicing method. The areas with a gray value below 15% were identified as void and marked in red in each figure, and their average areas were calculated. It is clear that the a-C:H films deposited under lower applied bias voltages of 0.20 and 0.30 kV exhibit looser nanostructures with larger size of nano-voids, while the films deposited under 0.50 kV show a denser structure. Figures 4(d)–4(f) show the ultrathin edges of micro-slices acquired by scratching the film surfaces with a diamond pin, and Figs. 4(g)–4(i) show the magnified views of the nanoclustering structures. The nanostructure of the films also evolved from loose to compact with the increase of bias voltage. In addition, it is noticeable that the a-C:H film deposited under 0.20 kV contains a number of multilayered spherical nanoclustering structures, as marked in blue in Figs. 4(d) and 4(f). To some extent, these nano-clustering structures show some similarities in morphology with the fullerene-like carbon films developed in Refs. [10, 69–71], but with the lower density of layered structure.

With the increase of bias voltage, these nanoclusters became harder to be identified, especially for the film of 0.50 kV. That is to say, under lower deposition energy, ion beam has a stronger tendency to form short-range-ordered, sphere-like, and layered nanoclustering structures with diameters of several nanometers. This phenomenon has a remarkable resemblance with the results of the simulations conducted by Ma et al. [72], in which the carbon ions with low injecting energies tend to form atomic strings or rings with low dimensional nanostructures. The interlamellar spacings of these layered nanoclusters were around 0.34 nm, which are close to those of multilayered graphene, hinting that these nanocluster structures were composed of curved graphite-like structures. On the contrary, higher ion energy tends to destroy these layered, sphere-like nanoclusters and form more disordered clustering structure with denser bonding architecture.

3.3 Bonding evolution governed by ion energy

The bonding states of a-C:H films were acquired by XPS and Raman characterization. For XPS analysis of

Fig. 4 TEM images of a-C:H films deposited under different bias voltages. (a–c) Thin nanoflake samples prepared by FIB slicing. The extracted nano voids and their mean area were marked in red. (d–f) Clustering structure of ultra-thin edges of micro-flakes acquired by pin-scratching. The layered and nanoclustering structures were marked in blue. (g–i) Polygon-like nanoclustering structures were found in the ultra-thin edges of micro-debris.

a-C:H films, the outermost ~ 10 nm layers were removed by low-energy Ar^+ sputtering to avoid any potential interference of surface contaminations and oxidization (which was estimated to be less than 1 nm by time-of-flight secondary ion mass spectrometry (TOF-SIMS) characterization [56]). Considering the relative intensities of C 1s, O 1s, and Si 2p peaks with their sensitivity factors, the impurities of oxygen and silicon in all the films were below 1%, which was considered to be negligible for C 1s peak fitting [73]. Figure 5(a) shows the C 1s spectra of a-C:H films. After subtracting a Shirley background, all the curves were precisely fitted with two Gaussian peaks located around 284.5 ± 0.1 and 285.3 ± 0.1 eV, in accordance with

sp^2 and sp^3 hybridized carbon, respectively [62, 74]. The sp^2 hybridization ratio then can be estimated from the area fraction of the two peaks [73, 75, 76], which is around 61%–65% for all the films.

For Raman characterization of a-C:H films, according to Casiraghi et al. [77], the Raman spectra of a-C:H films with higher hydrogen contents show stronger near-linear photoluminescence (PL) backgrounds. It is statistically convincible to evaluate the hydrogen content of highly-hydrogenated a-C:H film by comparing the intensity of G peak with the slope of PL background. The hydrogen ratios of a-C:H films deposited with a large variety of methods can be qualitatively predicted with Eq. (1) [77]:

Fig. 5 Structural analysis of a-C:H films. (a) XPS spectra of the a-C:H films deposited under different bias voltages; (b) element composition of the films; (c) Raman spectra of the films; (d) G peak position, width and relative intensity ratio of other peaks as a function of bias voltage; and (e) multiple peak fit of Raman spectra of a-C:H films.

$$H(\text{at}\%) = 21.7 + 16.6 \log \left(\frac{m}{I_G} (\mu\text{m}) \right) \quad (1)$$

where m is the slope of PL background between 1,050 and 1,800 cm⁻¹, and I_G is the intensity of G peak. Based on this knowledge, the element compositions of the a-C:H films can be evaluated, as shown in Fig. 5 (b). It is clear that, with the increase of deposition energy, the hydrogen content of a-C:H film shows a decreasing tendency. The a-C:H films deposited at low bias voltages between 0.20 and 0.30 kV were highly hydrogenated, showing an atomic ratio of hydrogen above 50%, which can be categorized into PLC [77]. Nevertheless, when the applied bias voltage increased to 0.35 kV, the hydrogen content of the film suddenly decreased to 38.7%. Furthermore, the a-C:H film deposited under 0.50 kV exhibited the lowest hydrogen content of 31.7%, which can be classified into DLC [77].

The Raman spectra of the a-C:H films after removing PL background and normalization are displayed in Fig. 5(c). Generally, all the spectra showed strong G-peaks around 1,545 cm⁻¹, which were derived from

the stretching vibration of double-bonded carbon atoms in both chains and rings [78]. The existence of D-peaks around 1,350 cm⁻¹ was also apparent for all the samples, which denoted the existence of the breathing vibration mode of carbon rings [78]. Different from the a-C:H films reported previously [23, 51, 79, 80], the present films exhibited a distinct peak around 1,227 cm⁻¹, especially for PLC films deposited under lower ion energies. Likewise, another peak around 1,458 cm⁻¹ also emerged for the a-C:H films deposited under the bias voltages below 0.30 kV. For the films deposited with low bias voltages, a weak peak around 1,020 cm⁻¹ was also distinguishable, but it disappeared with the elevated bias voltage.

The attribution of these peaks for carbon films is still controversial [81, 82]. For complicated amorphous carbon material, it is generally accepted that the peak at ~1,200 cm⁻¹ denotes the bonds between sp²-C and sp³-C atoms or C-C and C=C stretching vibrations of polyene-like structures [83–85], and the peak at ~1,500 cm⁻¹ originates from organic molecules, fragments, or functional groups [83, 86, 87]. For the present

films, considering their estimated hydrogen proportion and the aromatic precursor gaseous source, it is rational to assign the peaks to the ones similar with polymer materials containing phenyl ring. Interestingly, polystyrene also shows three distinct Raman peaks at around 1,000, 1,200, and 1,450 cm^{-1} [88–91]. The peak around 1,000 cm^{-1} was attributed to the breathing and symmetrical stretching vibration mode of benzene ring [90, 92]. The peak around 1,200 cm^{-1} was attributed to the stretching vibration mode between the phenyl rings and their attached carbon atoms in chains [92]. The peaks at around 1,450 cm^{-1} were broadly in-plane bending vibration modes of carbon and the toluene aromatic ring [88, 90, 92]. Thus, for the present a-C:H films, it is reasonable to deduce that the three peaks at 1,020, 1,227, and 1,458 cm^{-1} may originate from the polymer-like bonding structure containing phenyl rings or CH_2 chains, which might be from unfully-disintegrated radicals from toluene gas source. Another peak located at 1,670 cm^{-1} was also detected for low-energy-deposited PLC films. According to previous studies, this peak might result from the combination of $\text{C}=\text{O}$ stretching vibration peak around 1,700 cm^{-1} and the unpolymerized methacrylate peak at 1,640 cm^{-1} [46, 93, 94], which represented the oxidization of carbon.

According to the results, it is obvious that the shape of the Raman spectrum evolves with deposition bias voltage. The bias voltage of 0.30 kV seems to be a threshold deposition condition of two different types of a-C:H films in view of the obvious change in the shape of the Raman spectrum. Figure 5(d) shows the parameters subtracted from the results of multiple-peak fitting displayed in Fig. 5(e). As mentioned above, the G peak derives from stretching vibration of sp^2 carbon pairs from both chains or rings, and the dispersion of G peak position (labeled as P_G) can reflect the topological disorder or the reduction of cluster size (the effective chain conjugation length) of double bonds [77]. Obviously, the G peak position of a-C:H film has a significant tendency to move towards low wave number with increased bias voltage, especially when the deposition voltage reaching 0.35 kV. This phenomenon indicates that a higher deposition energy can restrict the size of clusters. Likewise, the full width at half maximum of G peak FWHM_G also increases with bias voltage and shows an abrupt

change at 0.35 kV. The width of G peak is an indicator for structural disorder of bond angle and length. The increase of this parameter indicates that the double bond cluster evolved from an unstrained, “molecular” state toward a distorted and disordered state [77, 78].

The lower graph of Fig. 5(d) shows the relative intensities of the Raman peaks as a function of bias voltage. It is noticeable that under low deposition energies, I_D , I_{1227} , and I_{1458} were relatively high, indicating that the film contains a large amount of ring structures originating from the incompletely disintegrated toluene gas source molecules. However, when the bias voltage increased from 0.20 to 0.35 kV, all of these peaks were restricted. Combining with the increase of G peak dispersion and G peak width, it can be deduced that the higher ion energy tends to destroy the aromatic ring structure from the gas source and re-establish topologically disordered bonding network. Interestingly, the oxidized carbon peak intensity I_{1670} also decreased with elevated bias voltage, which was nearly invisible at 0.35 kV. It is the speculation that the nano-porous and loose structure of a-C:H films deposited under low energies make themselves more vulnerable to surface oxidization when exposed to air or heated by laser.

3.4 Nanomechanical properties depending on ion energy

Figure 6 shows the mechanical properties of a-C:H films examined by nanoindentation. It is noticeable that the hardness of the film deposited under 0.20 kV was only 0.66 GP, similar to that of polymers. The hardness and elastic modules showed a piecewise linear increasing tendency with increased deposition energy, in which a sudden rise appeared between 0.25 and 0.30 kV as the hardness jumped from 1.65 to 4.64 GPa. In addition, the recovery rate of nano-indents also showed an increased tendency when the deposition energy increased from 0.20 to 0.30 kV. However, it was nearly a constant and exhibited a slightly decreasing tendency when the bias voltage further increased. The ratio between hardness and elastic modules (H/E , or plasticity index) was widely used to evaluate the coatings' ability to resist plastic deformation and mechanical wear [95]. It also showed a likewise tendency with recovery rate, which exhibited an optimized value at 0.30 kV.

Fig. 6 Nanomechanical properties of a-C:H films as a function of bias voltage.

Considering the characterization results of film bonding structure, it can be deduced that the enhanced hardness and elastic modulus were derived from a stiffer covalent network acquired from the higher deposition energy. When the deposition energy was low, the carbon skeleton was developed into a more “molecular”, chain-developed structure, which exhibited higher plasticity. Thus, to acquire a harder a-C:H film, an appropriate higher deposition energy was needed. Nevertheless, when it comes to the recovery rate of nanoindentation, it seems that a higher bias voltage above 0.30 kV did not show any more positive influences. The same was true for H/E ratio that a too high energy even led to a deteriorated plastic index. This phenomenon may result from the restricted nano-pores and the over cross-linked covalent network caused by the higher deposition energy, which could reduce the flexibility of carbon skeleton upon deformation.

4 Discussion

4.1 Mechanisms of structure evolution governed by ion energy

All the results above emphasize a fact that the bias voltage is a decisive factor affecting the tribological properties as well as the composition, bonding state, and nanoclustering structure of a-C:H film. The optimized superlubricity state in vacuum was achieved with the film deposited at 0.30 kV. Simultaneously, all the characterization results also hinted that there seems to be a critical voltage at about 0.30 kV, which allowed the nanostructure, bonding state, and mechanical properties of the films to be changed significantly. To understand the inherent influencing mechanism of bias

voltage on the superlubricity, the growth mechanism of a-C:H films depending on ion energy and its relation to the structure evolution of the films should be firstly discussed.

During the last three decades, multiple theories were brought up to explain the growth mechanism of DLC films [96]. It is widely accepted that the growing process of a-C:H in energetic gaseous environments is a combination of surface chemical process of neutrals or radicals and subsurface physical process of ion implantation [97]. As previously confirmed by mass spectrum analysis, during the ion beam deposition process, the gas source toluene (C_7H_8) was dominantly ionized into mono-radicals ($C_7H_7^+$), and accelerated by the electric field, forming an ion beam and bombarding on the sample surface. Theoretically, mono-radicals (with a magnitude of m_0) accelerated under a bias voltage of U will finally gain the highest kinetic energy of eU when reaching the sample. On the contact of the surface, after consuming an energy E_b to break the covalent bonds (which is calculated to be about 66 eV for the complete break up of $C_7H_7^+$), the radicals will break up into atomic ions with their kinetic energy re-distributed by their mass. In other words, the kinetic energy E_i for the atom with a magnitude of m_i could be roughly estimated by

$$E_i \approx \frac{m_i}{m_0} (eU - E_b) \quad (2)$$

Under this hypothesis, it can be calculated that the expected energy of impacted carbon atoms E_c was increased from 17.7 to 57.2 eV when the bias voltage was raised from 0.20 to 0.50 kV. The evolutions of film composition, bonding state, nanomechanical properties, and friction properties with increased carbon ion energy are summarized in Table 1. It is noticeable that the E_c was 30.9 eV when the bias voltage was 0.30 kV, which was exactly near the threshold energy for subplantation $E_p \approx 30$ eV predicted by simulations and experimental studies [4, 72, 98–100]. That is to say, when the bias voltage was below 0.30 kV, the growth mechanism of a-C:H films was dominated by surface chemical process of neutral species (C_7H_8) and nonradicals ($C_7H_7^+$) with the assistance of bombarding ions [97, 98]. When the applied bias voltage was higher than 0.30 kV, the carbon ions will have the chance to penetrate the atom interval

Table 1 Overview of parameters denoting film composition, bonding state, mechanical properties, and friction properties with elevated bias voltage and ion energy.

Bias voltage	Ion energy	Hydrogen content	G peak position	G Peak width	D peak ratio	Hardness	Recovery rate	Friction coefficient	Wear rate
U (kV)	E_C (eV)	(%)	P_G	$FWHM_G$	I_D/I_G	H (GPa)	R (%)	$\mu_{\min}$	($10^{-7} \text{ mm}^3 \cdot \text{N}^{-1} \cdot \text{m}^{-1}$)
0.20	17.7	54.3%	1549.1	92.4	0.794	0.67	45.65	0.033	367
0.25	24.3	53.3%	1548.4	94.2	0.662	1.15	67.35	0.016	66
0.30	30.9	50.8%	1547.7	112.2	0.406	4.64	80.65	0.007	12
0.35	37.5	38.7%	1535.2	154.4	0.345	5.41	80.67	0.008	672
0.40	44.0	37.2%	1534.6	157.8	0.347	5.93	81.67	0.008	787
0.50	57.2	31.7%	1534.3	162.7	0.366	7.25	77.71	0.012	1,612

on the surface, inject into the sublayer of the films, and bond with local carbon ions [101, 102].

Figure 7 shows the schematic of the proposed growth model of a-C:H films with toluene gas source. During the deposition process, negatively-charged dangling bonds are continually generated on the surface due to the bombarding of ion beam and the applied bias voltage. As a consequence of the inhibition of the neutral molecules or insufficient acceleration due to the pulsed bias voltage, a noticeable amount of low-energy positive radicals of C_7H_7^+ as well as their crashed debris exists around the sample surface. These radicals are energetically preferential to chemisorb on the terminals [97], forming chain-developed polymer-like nanoclustering structure. The chemisorb growth mode should be the dominant growth mechanism when the bias voltage was below 0.30 kV, which was also proved by the graininess surface morphology and ring-like nano-clusters, as shown in Figs. 3(b) and 4(d), respectively. As shown in Figs. 5(c)–5(e), under low deposition energy, the existence of distinct Raman peaks at 1,227 and 1,458 cm^{-1} further indicates that a large number of toluene molecules were chemically incorporated into the films without full decomposition, forming chain developed polymer-like bonding structure.

When the bias voltage is higher than 0.30 kV, a number of carbon ions can gain enough kinetic energy to penetrate surface and replace carbon atoms at sublayer, which might break the local aromatic ring and chain-developed structure. This process can be confirmed by the decrease of Raman peak intensities of I_D as well as the sudden deviation of G peak position

Fig. 7 Schematic of deposition mechanism of PLC films.

(as shown in Figs. 5(c)–5(e)), denoting the restrain of ring structures and the reduction of clustering size of sp^2 -hybridized carbon. Meanwhile, the decrease of I_{1227} and I_{1458} also implies that the benzene rings and chain-developed structures were replaced by spatially-developed cross-linked network. This hypothesis can also explain the structure evolution detected by AFM and TEM, as shown in Figs. 3 and 4, respectively. On the top surface of the growing film, the bombarding process of high energy ions can erode the hills into neighboring hollows via the impact-induced downhill currents [68], which polished the rough, grainy morphology grown from chemisorption into a flattened, network-like morphology (as shown in Fig. 3) [66, 67]. Simultaneously, the subsurface implanted ions can restrict the nanoclusters structure originating from the growth mode of surface chemical adsorbing (as shown in Fig. 4), and form a more dense, disordered bonding network. As a consequence of the enhanced nano-clustering structure and compact bonding network, the

hardness and elastic modules suddenly increased at 0.30 kV, as shown in Fig. 6. However, the side effect of implantation is that the injected carbon ions can cause hydrogen detachment by preferentially displacing C–H bonds with C–C bonds [97]. As shown in Fig. 5(b), with elevated bias voltage, a sudden decrease of the calculated hydrogen content from 50.8% to 38.7% happened at 0.35 kV when E_c increased to 37.5 eV, which is significantly higher than 30 eV. In conclusion, a higher ion energy is needed to form robust bonding network, while a relatively low energy is necessary for reserving a mass of hydrogen atoms. The optimal combination of the film mechanical toughness and the chemical passivation ability is the key for designing deposition energy.

Interestingly, when comparing with a-C:H films in previous research, it seems that the structural evolution pathway with increased hydrogen content also shows dependence on the gaseous source. Figure 8 shows the structural diagram of the previously reported amorphous carbon films (marked as a blue background [60, 103, 104]) and the present synthesized films (marked with a red arrow denoting the structure evolution pathway with the elevated hydrogen content). For traditional a-C:H films grown from hydrogen, alkane, olefin, or alkyne, with the elevated hydrogen proportion, the fraction of sp^2 phase exhibits an apparent decreasing tendency [60, 104]. It is noticeable that the a-C:H

films synthesized with toluene could keep a high sp^2 hybridization rate even though the hydrogen proportion was approaching 50%. This particularity may originate from the stronger resisting ability against the addition reaction of benzene, which enabled a-C:H film to preserve a quantity of hydrogen atoms in aromatic ring structure without losing sp^2 -hybridized carbon atoms.

4.2 Super-low friction and wear achieved with a-C:H films depending on ion energy

The question of how the deposition energy influencing tribological behavior of a-C:H films, fundamentally, is the question of how the ion-energy-induced bonding structure influencing the self-lubrication mechanisms of a-C:H films. As shown in Fig. 1, only 0.30 kV voltage can lead to robust superlubricity state, while too high or too low bias voltages can both deteriorate the anti-wear property. The inherent mechanisms should be multifaceted.

Though the films deposited at 0.35–0.50 kV exhibited an increasing hardness and elastic modulus, their anti-wear property and duration of super-low friction state were unsatisfying. This deficiency was due to the insufficient hydrogen content deriving from the high ion energy. Surface hydrogen passivation is widely accepted to be the most essential factor for the establishment of a non-adhesive sliding surface with ultralow friction and wear [24, 25, 27, 105]. It is believed that most hydrogen atoms in a-C:H films are chemically bonded with carbon atoms, while some of the hydrogen atoms remain unbonded in the form of single H_2 molecules or incompletely disintegrated gas source molecule and physically trapped in the voids of bonding network [34]. When a-C:H films were tribo-tested under dry sliding condition, hydrogen can be detected to be released from the films in the form of H_2 and alkanes [106, 107]. During the sliding contact, surface dangling bonds should be continuously generated due to tribochemical interactions, which have potential to form covalent bonds bridging counterpart surfaces, resulting in high friction and wear [108, 109]. Nevertheless, a well supply of hydrogen from the films can timely passivate these exposed dangling bonds and reduce their occurrence, forming a non-adhesive sliding surface [110–112]. Due to the electron transfer of C–H dipole enabled by the low electronegativity of hydrogen atom,

Fig. 8 Structural diagram of the amorphous carbon films. The blue background shows the DLC films in previous studies, and the red arrow shows the present a-C:H films synthesized in this work. The structure evolution tendency passed a blank region of traditional ternary phase diagram of DLC material system. Reproduced with permission from Ref. [6]. © Elsevier, 2007.

the hydrogen terminations on sliding surfaces are positively charged and repulse each other via dipole-dipole force, which further reduce the interaction between contact surfaces and leading to ultralow friction and wear [113, 114].

Abundant hydrogen contained in the film plays a critical role in achieving a robust superlubricity state, especially in vacuum, where the protective effect of the physical adsorption layer and the heat convection effect by means of gaseous molecules do not exist anymore. Meanwhile, the relatively high mean free path of molecules in vacuum also accelerates the dissipation of hydrogen atoms in the contact area. Thus, the wear rate of a-C:H films in vacuum is one or two magnitudes higher than that in air or dry nitrogen environment [36, 38, 64, 65], mainly due to the chemically adhesive effect caused by hydrogen detachment. As shown in Figs. 5(b) and 1(b), when the bias increased from 0.30 to 0.35 kV, a significant decrease of hydrogen content from ~51% to ~39% happened due to ion subplantation, which led to a restricted surface passivation ability of the films and a sudden increase in wear rate, from 1.21×10^{-6} to $6.72 \times 10^{-5} \text{ mm}^3 \cdot \text{N}^{-1} \cdot \text{m}^{-1}$. The same was true with the films deposited at 0.40 and 0.50 kV that their increased wear rates were coupled with their decreased hydrogen content. Thus, for establishing robustly-passivated sliding surfaces in vacuum, it is advisable to trap as more hydrogen as possible inside the film during deposition, which can be realized by reducing the ion energy and enhancing chemical growth mode during deposition.

However, when the ion energy decreased from 0.30 to 0.25 kV, the a-C:H films lost their superlubricity property and also showed an increased wear rate from 1.21×10^{-6} to $6.57 \times 10^{-6} \text{ mm}^3 \cdot \text{N}^{-1} \cdot \text{m}^{-1}$, despite their high hydrogen rates are around 50% (as shown in Figs. 1 and 5(b), respectively). Under these circumstances, the mechanical properties should be taken into consideration, which should be the precondition for the establishment of stable passivated sliding surfaces [2, 34]. As shown in Fig. 6, the H/E ratio of the film as well as the recovery rate of indentation significantly decreased when the bias voltage was below 0.30 kV, which was in accordance with the restricted anti-wear properties of the films. For establishing stable self-lubricating state, an appropriate hardness was needed

for the films to resist the asperities of the counterparts against pressing in, which could reduce the energy dissipation and material dislocation caused by the plastic flow of the material and lead to low friction and wear [103]. In addition, some researchers believe that the superlubricity property of a-C:H films is also attributed to the easy-searing graphene-like layered structure, which is generated from the rehybridization of sp^3 spatial network during friction contact [24, 48, 53, 56, 115]. Under this hypothesis, the barrier to achieve superlubricity for a-C:H films deposited under low energy may also be related to their chain-developed, passivated bonding structures, which could hamper the surface structure evolution towards the graphene-like layered structure. Consequently, sufficient mechanical stiffness induced by the spatial network bonding structure is also necessary for the films to acquire the optimized self-lubricative and anti-wear ability, which can be realized by subplantation growth model enabled by the higher ion energy.

Thus, for achieving a robust superlubricity in vacuum, the optimized combination of the surface passivation ability and the mechanical stiffness of the films is of vital importance, which could be tailored by adjusting the ion energy to approach the surface penetration threshold of carbon ions. For the IBD synthesis method with toluene in this study, the deposition energy of 0.30 kV exactly met this requirement. The growth activity is that the corresponding carbon ion energy is exactly near the surface penetration threshold around 30 eV. As a consequence, this deposition energy leads to an appropriately combined growth mode of both surface chemical adsorption and subsurface implantation. On the one hand, the chain-developed polymeric structure originating from chemical adsorption provides an effective carriage of hydrogen to passivate the sliding surface. On the other hand, the moderately-implanted ions appropriately cross-link the nanoclustering network and enhance the mechanical properties to resist plastic flow. These two factors work together, and enable the a-C:H film to eliminate the two main origins of friction, abrasion, and adhesion simultaneously, thus leading to the optimized superlubricity state and the highest anti-wear property in vacuum, with the lowest friction coefficient of 0.006 and a wear rate of $1.21 \times 10^{-6} \text{ mm}^3 \cdot \text{N}^{-1} \cdot \text{m}^{-1}$.

These findings highlight the important relationships between subplantation energy and superlubricity of a-C:H films, which can provide guidance for the design of self-lubricating carbon films for the applications in space or other extreme environments.

5 Conclusions

In this study, the optimized superlubricity state in vacuum was achieved by adjusting the deposition ion energy of a-C:H, and the influencing mechanism of ion energy on the superlubricity of a-C:H was investigated. The tribological experiments show that the most suitable level of bias voltage for synthesizing superlubricous a-C:H was exactly in accordance with the surface penetrations threshold of carbon ions, and the characterization results highlighted the importance of the growth modes governed by ion energy, which ultimately determines the nanoclustering structure, element composition, bonding state, and mechanical properties of the films. The suitable combination of chemically-grown chain-developed hydrogen-rich bonding structure and the subplantation-enhanced bonding network eliminated the surface adhesion effect and abrasion effect simultaneously, which led to the optimized superlubricity state in vacuum. These findings can provide a guidance for the design and manufacture of superior self-lubricating carbon films for engineering applications in vacuum or extreme working conditions.

Acknowledgements

The authors would like to thank Dongzhou ZHAN for technological support during friction experiment. This work was supported by the National Natural Science Foundation of China (Nos. 51925506, 51975314, 51935006, and 51527901).

Open Access This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons licence, and indicate if changes were made.

The images or other third party material in this

article are included in the article's Creative Commons licence, unless indicated otherwise in a credit line to the material. If material is not included in the article's Creative Commons licence and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder.

To view a copy of this licence, visit <http://creativecommons.org/licenses/by/4.0/>.

References

- [1] Enke K. Some new results on the fabrication of and the mechanical, electrical and optical properties of i-carbon layers. *Thin Solid Films* **80**(1–3): 227–234 (1981)
- [2] Fontaine J, Loubet J L, Mogne T L, Grill A. Superlow friction of diamond-like carbon films: A relation to viscoplastic properties. *Tribol Lett* **17**(4): 709–714 (2004)
- [3] Tyagi A, Walia R S, Murtaza Q, Pandey S M, Tyagi P K, Bajaj B. A critical review of diamond like carbon coating for wear resistance applications. *Int J Refract Met Hard Mater* **78**: 107–122 (2019)
- [4] Hauert R, Müller U. An overview on tailored tribological and biological behavior of diamond-like carbon. *Diam Relat Mater* **12**(2): 171–177 (2003)
- [5] Erdemir A, Donnet C. Tribology of diamond-like carbon films: Recent progress and future prospects. *J Phys D: Appl Phys* **39**(18): R311–R327 (2006)
- [6] Casiraghi C, Robertson J, Ferrari A C. Diamond-like carbon for data and beer storage. *Mater Today* **10**(1–2): 44–53 (2007)
- [7] Luo J B, Zhou X. Superlubricative engineering—Future industry nearly getting rid of wear and frictional energy consumption. *Friction* **8**(4): 643–665 (2020)
- [8] Fan X Q, Xue Q J, Wang L P. Carbon-based solid-liquid lubricating coatings for space applications-A review. *Friction* **3**(3): 191–207 (2015)
- [9] Sutton D C, Limbert G, Stewart D, Wood R J K. The friction of diamond-like carbon coatings in a water environment. *Friction* **1**(3): 210–221 (2013)
- [10] Jia Q, Gao K, An Y, Zhang B, Bai C, Wang Z, Zhang J. Fullerene-like structure hydrogenated carbon film: One way to the industrial scale superlubricity. In *Prime Archives in Material Science*. Heimann R B, Ed. Hyderabad: Vide Leaf, 2020: 1–26
- [11] Ohtake N, Hiratsuka M, Kanda K, Akasaka H, Tsujioka M, Hirakuri K, Hirata A, Ohana T, Inaba H, Kano M, et al. Properties and classification of diamond-like carbon films. *Materials* **14**(2): 315 (2021)

- [12] Bai C N, Gong Z B, An L L, Qiang L, Zhang J Y, Yushkov G, Nikolaev A, Shandrikov M, Zhang B. Adhesion and friction performance of DLC/rubber: The influence of plasma pretreatment. *Friction* 9(3): 627–641 (2021)
- [13] Liu K, Kang J J, Zhang G A, Lu Z B, Yue W. Effect of temperature and mating pair on tribological properties of DLC and GLC coatings under high pressure lubricated by MoDTC and ZDDP. *Friction* 9(6): 1390–1405 (2021)
- [14] Braceras I, Ibáñez I, Dominguez-Meister S, Velasco X, Brizuela M, Garmendia I. Electro-tribological properties of diamond like carbon coatings. *Friction* 8(2): 451–461 (2020)
- [15] Li K S, Xu G, Wen X B, Zhou J, Gong F. High-temperature friction behavior of amorphous carbon coating in glass molding process. *Friction* 9(6): 1648–1659 (2021)
- [16] Shi P F, Sun J H, Liu Y H, Zhang B, Zhang J Y, Chen L, Qian L M. Running-in behavior of a H-DLC/Al₂O₃ pair at the nanoscale. *Friction* 9(6): 1464–1473 (2021)
- [17] Gongyang Y J, Ouyang W G, Qu C Y, Urbakh M, Quan B G, Ma M, Zheng Q S. Temperature and velocity dependent friction of a microscale graphite–DLC heterostructure. *Friction* 8(2): 462–470 (2020)
- [18] Jang Y J, Kim J I, Lee W, Kim J. Tribological properties of multilayer tetrahedral amorphous carbon coatings deposited by filtered cathodic vacuum arc deposition. *Friction* 9(5): 1292–1302 (2021)
- [19] Zhong M, Zhang C H, Luo J B, Lu X C. The protective properties of ultra-thin diamond like carbon films for high density magnetic storage devices. *Appl Surf Sci* 256(1): 322–328 (2009)
- [20] Donnet C, Belin M, Augé J C, Martin J M, Grill A, Patel V. Tribochemistry of diamond-like carbon coatings in various environments. *Surf Coat Technol* 68–69: 626–631 (1994)
- [21] Donnet C, Grill A. Friction control of diamond-like carbon coatings. *Surf Coat Technol* 94–95: 456–462 (1997)
- [22] Erdemir A, Eryilmaz O L, Nilufer I B, Fenske G R. Effect of source gas chemistry on tribological performance of diamond-like carbon films. *Diam Relat Mater* 9(3–6): 632–637 (2000)
- [23] Erdemir A, Eryilmaz O L, Nilufer I B, Fenske G R. Synthesis of superlow-friction carbon films from highly hydrogenated methane plasmas. *Surf Coat Technol* 133–134: 448–454 (2000)
- [24] Chen X C, Li J J. Superlubricity of carbon nanostructures. *Carbon* 158: 1–23 (2020)
- [25] Yu Q Y, Chen X C, Zhang C H, Luo J B. Influence factors on mechanisms of superlubricity in DLC films: A review. *Front Mech Eng* 6: 65 (2020)
- [26] Baykara M Z, Vazirisereshk M R, Martini A. Emerging superlubricity: A review of the state of the art and perspectives on future research. *Appl Phys Rev* 5(4): 041102 (2018)
- [27] Erdemir A, Eryilmaz O. Achieving superlubricity in DLC films by controlling bulk, surface, and tribochemistry. *Friction* 2(2): 140–155 (2014)
- [28] Erdemir A, Eryilmaz O L. 16-Superlubricity in diamondlike carbon films. In *Superlubricity*. Erdemir A, Martin J, Ed. Amsterdam: Elsevier Science B.V., 2007: 253–271
- [29] Fontaine J, Le Mogne T, Loubet J L, Belin M. Achieving superlow friction with hydrogenated amorphous carbon: Some key requirements. *Thin Solid Films* 482(1–2): 99–108 (2005)
- [30] Liu S W, Zhang C H, Osman E, Chen X C, Ma T B, Hu Y Z, Luo J B, Ali E. Influence of tribofilm on superlubricity of highly-hydrogenated amorphous carbon films in inert gaseous environments. *Sci China Technol Sci* 59(12): 1795–1803 (2016)
- [31] Meng Y G, Xu J, Jin Z M, Prakash B, Hu Y Z. A review of recent advances in tribology. *Friction* 8(2): 221–300 (2020)
- [32] Cao Z Y, Zhao W W, Liang A M, Zhang J Y. A general engineering applicable superlubricity: Hydrogenated amorphous carbon film containing nano diamond particles. *Adv Mater Interfaces* 4(14): 1601224 (2017)
- [33] Sui X D, Wang X Y, Zhang S T, Yan M M, Li W S, Hao J Y, Liu W M. Nano-twisted double helix carbon debris improves the wear resistance of ultra-thick diamond-like carbon coatings. *Adv Mater Interfaces* 7(20): 2000857 (2020)
- [34] Erdemir A. Genesis of superlow friction and wear in diamondlike carbon films. *Tribol Int* 37(11–12): 1005–1012 (2004)
- [35] Donnet C. Recent progress on the tribology of doped diamond-like and carbon alloy coatings: A review. *Surf Coat Technol* 100–101: 180–186 (1998)
- [36] Vanhulsel A, Velasco F, Jacobs R, Eersels L, Havermans D, Roberts E W, Sherrington I, Anderson M J, Gaillard L. DLC solid lubricant coatings on ball bearings for space applications. *Tribol Int* 40(7): 1186–1194 (2007)
- [37] Donnet C, Fontaine J, Le Mogne T, Belin M, Héau C, Terrat J P, Vaux F, Pont G. Diamond-like carbon-based functionally gradient coatings for space tribology. *Surf Coat Technol* 120–121: 548–554 (1999)
- [38] Vercammen K, Meneve J, Dekempeneer E, Smeets J, Roberts E W, Eiden M J. Study of RF PACVD diamond-like carbon coatings for space mechanism applications. *Surf Coat Technol* 120–121: 612–617 (1999)
- [39] Andersson J, Erck R A, Erdemir A. Frictional behavior of diamondlike carbon films in vacuum and under varying water vapor pressure. *Surf Coat Technol* 163–164: 535–540 (2003)

- [40] Moolsradoo N, Watanabe S. Modification of tribological performance of DLC films by means of some elements addition. *Diam Relat Mater* **19**(5–6): 525–529 (2010)
- [41] Liu X F, Wang L P, Xue Q J. A novel carbon-based solid-liquid duplex lubricating coating with super-high tribological performance for space applications. *Surf Coat Technol* **205**(8–9): 2738–2746 (2011)
- [42] Wang Y F, Wang J, Zhang G G, Wang L P, Yan P X. Microstructure and tribology of TiC(Ag)/a-C: H nanocomposite coatings deposited by unbalanced magnetron sputtering. *Surf Coat Technol* **206**(14): 3299–3308 (2012)
- [43] Fontaine J, Donnet C, Grill A, LeMogne T. Tribochemistry between hydrogen and diamond-like carbon films. *Surf Coat Technol* **146–147**: 286–291 (2001)
- [44] Chen X C, Kato T, Nosaka M. Origin of superlubricity in a-C:H:Si films: A relation to film bonding structure and environmental molecular characteristic. *ACS Appl Mater Interfaces* **6**(16): 13389–13405 (2014)
- [45] Zhang S L, Wagner G, Medyanik S N, Liu W K, Yu Y H, Chung Y W. Experimental and molecular dynamics simulation studies of friction behavior of hydrogenated carbon films. *Surf Coat Technol* **177–178**: 818–823 (2004)
- [46] Cui L C, Zhou H, Zhang K F, Lu Z B, Wang X R. Bias voltage dependence of superlubricity lifetime of hydrogenated amorphous carbon films in high vacuum. *Tribol Int* **117**: 107–111 (2018)
- [47] Liu Y, Erdemir A, Meletis E I. An investigation of the relationship between graphitization and frictional behavior of DLC coatings. *Surf Coat Technol* **86–87**: 564–568 (1996)
- [48] Chen X C, Zhang C H, Kato T, Yang X A, Wu S D, Wang R, Nosaka M, Luo J B. Evolution of tribo-induced interfacial nanostructures governing superlubricity in a-C:H and a-C:H:Si films. *Nat Commun* **8**(1): 1675 (2017)
- [49] Liu Y, Meletis E I. Evidence of graphitization of diamond-like carbon films during sliding wear. *J Mater Sci* **32**(13): 3491–3495 (1997)
- [50] Scharf T W, Singer I L. Quantification of the thickness of carbon transfer films using Raman tribometry. *Tribol Lett* **14**(2): 137–145 (2003)
- [51] Sánchez-López J C, Erdemir A, Donnet C, Rojas T C. Friction-induced structural transformations of diamondlike carbon coatings under various atmospheres. *Surf Coat Technol* **163–164**: 444–450 (2003)
- [52] Tambe N S, Bhushan B. Nanoscale friction-induced phase transformation of diamond-like carbon. *Scripta Mater* **52**(8): 751–755 (2005)
- [53] Ma T B, Wang L F, Hu Y Z, Li X, Wang H. A shear localization mechanism for lubricity of amorphous carbon materials. *Sci Rep* **4**: 3662 (2014)
- [54] Ma T B, Hu Y Z, Wang H. Molecular dynamics simulation of shear-induced graphitization of amorphous carbon films. *Carbon* **47**(8): 1953–1957 (2009)
- [55] Wang Y, Xu J X, Zhang J, Chen Q, Ootani Y, Higuchi Y, Ozawa N, Martin J M, Adachi K, Kubo M. Tribochemical reactions and graphitization of diamond-like carbon against alumina give volcano-type temperature dependence of friction coefficients: A tight-binding quantum chemical molecular dynamics simulation. *Carbon* **133**: 350–357 (2018)
- [56] Wang K, Zhang J, Ma T B, Liu Y M, Song A S, Chen X C, Hu Y Z, Carpick R W, Luo J B. Unraveling the friction evolution mechanism of diamond-like carbon film during nanoscale running-in process toward superlubricity. *Small* **17**(1): 2005607 (2021)
- [57] Huai W J, Zhang C H, Wen S Z. Graphite-based solid lubricant for high-temperature lubrication. *Friction* **9**(6): 1660–1672 (2021)
- [58] Hu Z L, Fan X, Chen C. Multiscale frictional behaviors of sp² nanocrystallized carbon films with different ion irradiation densities. *Friction* **9**(5): 1025–1037 (2021)
- [59] Tian H L, Wang C L, Guo M Q, Cui Y J, Gao J G, Tang Z H. Microstructures and high-temperature self-lubricating wear-resistance mechanisms of graphene-modified WC–12Co coatings. *Friction* **9**(2): 315–331 (2021)
- [60] Weiler M, Sattel S, Giessen T, Jung K, Ehrhardt H, Veerasamy V S, Robertson J. Preparation and properties of highly tetrahedral hydrogenated amorphous carbon. *Phys Rev B Condens Matter* **53**(3): 1594–1608 (1996)
- [61] Chen X C, Kato T, Kawaguchi M, Nosaka M, Choi J. Structural and environmental dependence of superlow friction in ion vapour-deposited a-C:H:Si films for solid lubrication application. *J Phys D: Appl Phys* **46**(25): 255304 (2013)
- [62] Chen X C, Kato T. Growth mechanism and composition of ultrasmooth a-C:H:Si films grown from energetic ions for superlubricity. *J Appl Phys* **115**(4): 044908 (2014)
- [63] Weissmantel C, Reisse G, Erler H J, Henny F, Bewilogua K, Ebersbach U, Schürer C. Preparation of hard coatings by ion beam methods. *Thin Solid Films* **63**(2): 315–325 (1979)
- [64] Aggleton M, Burton J C, Taborek P. Cryogenic vacuum tribology of diamond and diamond-like carbon films. *J Appl Phys* **106**(1): 013504 (2009)
- [65] Miyoshi K. Lubrication by diamond and diamondlike carbon coatings. *J Tribol* **120**(2): 379–384 (1998)
- [66] Lopez-Santos C, Colaux J L, Gonzalez J C, Lucas S. Investigation of the growth mechanisms of a-CH_x coatings

- deposited by pulsed reactive magnetron sputtering. *J Phys Chem C* **116**(22): 12017–12026 (2012)
- [67] Vázquez L, Buijnsters J G. Chemical and physical sputtering effects on the surface morphology of carbon films grown by plasma chemical vapor deposition. *J Appl Phys* **106**(3): 033504 (2009)
- [68] Moseler M, Gumbsch P, Casiraghi C, Ferrari AC, Robertson J. The ultrasmoothness of diamond-like carbon surfaces. *Science* **309**(5740): 1545–1548 (2005)
- [69] Wang J, Zhang K, Zhang L, Wang F, Zhang J, Zheng W. Influence of structure evolution on tribological properties of fluorine-containing diamond-like carbon films: From fullerene-like to amorphous structures. *Appl Surf Sci* **457**: 388–395 (2018)
- [70] Wang Q, Wang C B, Wang Z, Zhang J Y, He D Y. Fullerene nanostructure-induced excellent mechanical properties in hydrogenated amorphous carbon. *Appl Phys Lett* **91**(14): 141902 (2007)
- [71] Wang C B, Yang S R, Wang Q, Wang Z, Zhang J Y. Super-low friction and super-elastic hydrogenated carbon films originated from a unique fullerene-like nanostructure. *Nanotechnology* **19**(22): 225709 (2008)
- [72] Ma T B, Hu Y Z, Wang H, Li X. Microstructural and stress properties of ultrathin diamondlike carbon films during growth: Molecular dynamics simulations. *Phys Rev B* **75**(3): 035425 (2007)
- [73] Haerle R, Riedo E, Pasquarello A, Baldereschi A. sp^2/sp^3 hybridization ratio in amorphous carbon from C 1s core-level shifts: X-ray photoelectron spectroscopy and first-principles calculation. *Phys Rev B* **65**(4): 045101 (2001)
- [74] Paik N. Raman and XPS studies of DLC films prepared by a magnetron sputter-type negative ion source. *Surf Coat Technol* **200**(7): 2170–2174 (2005)
- [75] Dey R M, Pandey M, Bhattacharyya D, Patil D S, Kulkarni S K. Diamond like carbon coatings deposited by microwave plasma CVD: XPS and ellipsometric studies. *Bull Mater Sci* **30**(6): 541–546 (2007)
- [76] Ferro S, Dal Colle M, De Battisti A. Chemical surface characterization of electrochemically and thermally oxidized boron-doped diamond film electrodes. *Carbon* **43**(6): 1191–1203 (2005)
- [77] Casiraghi C, Ferrari A C, Robertson J. Raman spectroscopy of hydrogenated amorphous carbons. *Phys Rev B* **72**(8): 085401 (2005)
- [78] Cheng G X, Guo S L, He Y L, Wang Z C. Raman spectroscopy on hydrogenated amorphous carbon. *Vacuum* **42**(16): 1084 (1991)
- [79] Johnson J A, Woodford J B, Chen X D, Andersson J, Erdemir A, Fenske G R. Insights into “near-frictionless carbon films”. *J Appl Phys* **95**(12): 7765–7771 (2004)
- [80] Arenal R, Liu A C Y. Clustering of aromatic rings in near-frictionless hydrogenated amorphous carbon films probed using multiwavelength Raman spectroscopy. *Appl Phys Lett* **91**(21): 211903 (2007)
- [81] Wang C B, Yang S R, Li H X, Zhang J Y. Elastic properties of a-C:N:H films. *J Appl Phys* **101**(1): 013501 (2007)
- [82] Piazza F, Schulze S, Relihan G, Golanski A. Transpolyacetylene chains in DECR plasma deposited a-C:H films. *Diam Relat Mater* **12**(3–7): 942–945 (2003)
- [83] Sadezky A, Muckenhuber H, Grothe H, Niessner R, Pöschl U. Raman microspectroscopy of soot and related carbonaceous materials: Spectral analysis and structural information. *Carbon* **43**(8): 1731–1742 (2005)
- [84] Dippel B, Heintzenberg J. Soot characterization in atmospheric particles from different sources by NIR FT Raman spectroscopy. *J Aerosol Sci* **30**: S907–S908 (1999)
- [85] Dippel B, Jander H, Heintzenberg J. NIR FT Raman spectroscopic study of flame soot. *Phys Chem Chem Phys* **1**(20): 4707–4712 (1999)
- [86] Cuesta A, Dhamelincourt P, Laureyns J, Martínez-Alonso A, Tascón J M D. Raman microprobe studies on carbon materials. *Carbon* **32**(8): 1523–1532 (1994)
- [87] Jawhari T, Roid A, Casado J. Raman spectroscopic characterization of some commercially available carbon black materials. *Carbon* **33**(11): 1561–1565 (1995)
- [88] Musto P, Borriello A, Agoretti P, Napolitano T, Florio G D, Mensitieri G. Selective surface modification of syndiotactic polystyrene films: A study by Fourier transform- and confocal-Raman spectroscopy. *Eur Polym J* **46**(5): 1004–1015 (2010)
- [89] Jones C H, Wesley I J. A preliminary study of the Fourier transform Raman spectra of polystyrenes. *Spectrochimica Acta A: Mol Spectrosc* **47**(9–10): 1293–1298 (1991)
- [90] Signer R, Weiler J. Raman-Spektrum und Konstitution hochmolekularer Stoffe. 62. Mitteilung über hochpolymere Verbindungen. *Helvetica Chimica Acta* **15**(1): 649–657 (1932)
- [91] Torres F J, Civalleri B, Meyer A, Musto P, Albuñia A R, Rizzo P, Guerra G. Normal vibrational analysis of the syndiotactic polystyrene $s(2/1)_2$ helix. *J Phys Chem B* **113**(15): 5059–5071 (2009)
- [92] Tasumi M, Urano T, Nakata M. Some thoughts on the vibrational modes of toluene as a typical monosubstituted benzene. *J Mol Struct* **146**: 383–396 (1986)
- [93] Leloup G, Holvoet P E, Bebelman S, Devaux J. Raman scattering determination of the depth of cure of light-activated composites: Influence of different clinically relevant parameters. *J Oral Rehabilitation* **29**(6): 510–515 (2002)

- [94] Zhu W L, Arao K, Nakamura M, Takagawa Y, Miura K I, Kobata J, Marin E, Pezzotti G. Raman spectroscopic studies of stress-induced structure alteration in diamond-like carbon films. *Diam Relat Mater* **94**: 1–7 (2019)
- [95] Leyland A, Matthews A. On the significance of the H/E ratio in wear control: A nanocomposite coating approach to optimised tribological behaviour. *Wear* **246**(1–2): 1–11 (2000)
- [96] Hofsäss H, Feldermann H, Merk R, Sebastian M, Ronning C. Cylindrical spike model for the formation of diamondlike thin films by ion deposition. *Appl Phys A* **66**(2): 153–181 (1998)
- [97] Robertson J. Diamond-like amorphous carbon. *Mater Sci Eng: R: Rep* **37**(4–6): 129–281 (2002)
- [98] Uhlmann S, Frauenheim T, Lifshitz Y. Molecular-dynamics study of the fundamental processes involved in subplantation of diamondlike carbon. *Phys Rev Lett* **81**(3): 641–644 (1998)
- [99] Koponen I, Hakovirta M, Lappalainen R. Modeling the ion energy dependence of the sp^3/sp^2 bonding ratio in amorphous diamondlike films produced with a mass-separated ion beam. *J Appl Phys* **78**(9): 5837–5839 (1995)
- [100] Lifshitz Y, Lempert G D, Grossman E, Avigal I, Uzan-Saguy C, Kalish R, Kulik J, Marton D, Rabalais J W. Growth mechanisms of DLC films from C^+ ions: Experimental studies. *Diam Relat Mater* **4**(4): 318–323 (1995)
- [101] Robertson J. Mechanism of sp^3 bond formation in the growth of diamond-like carbon. *Diam Relat Mater* **14**(3–7): 942–948 (2005)
- [102] Lifshitz Y, Kasi S R, Rabalais J W. Subplantation model for film growth from hyperthermal species: Application to diamond. *Phys Rev Lett* **62**(11): 1290–1293 (1989)
- [103] Donnet C, Erdemir A. *Tribology of Diamond-like Carbon Films: Fundamentals and Applications*. New York (USA): Springer, 2008.
- [104] Jacob W, Möller W. On the structure of thin hydrocarbon films. *Appl Phys Lett* **63**(13): 1771–1773 (1993)
- [105] Romero P A, Pastewka L, Von Lautz J, Moseler M. Surface passivation and boundary lubrication of self-mated tetrahedral amorphous carbon asperities under extreme tribological conditions. *Friction* **2**(2): 193–208 (2014)
- [106] Nevshupa R, Caro J, Arratibel A, Bonet R, Rusanov A, Ares J R, Roman E. Evolution of tribologically induced chemical and structural degradation in hydrogenated a-C coatings. *Tribol Int* **129**: 177–190 (2019)
- [107] Wang Y, Yamada N, Xu J, Zhang J, Chen Q, Ootani Y, Higuchi Y, Ozawa N, Bouchet MB, Martin JM, et al. Triboemission of hydrocarbon molecules from diamond-like carbon friction interface induces atomic-scale wear. *Sci Adv* **5**(11): eaax9301 (2019)
- [108] Schall J D, Gao G T, Harrison J A. Effects of adhesion and transfer film formation on the tribology of self-mated DLC contacts. *J Phys Chem C* **114**(12): 5321–5330 (2010)
- [109] Zhao S J, Zhang Z H, Wu Z H, Liu K H, Zheng Q S, Ma M. The impacts of adhesion on the wear property of graphene. *Adv Mater Interfaces* **6**(18): 1900721 (2019)
- [110] Erdemir A. The role of hydrogen in tribological properties of diamond-like carbon films. *Surf Coat Technol* **146–147**: 292–297 (2001)
- [111] Pastewka L, Moser S, Moseler M, Blug B, Meier S, Hollstein T, Gumbsch P. The running-in of amorphous hydrocarbon tribocoatings: A comparison between experiment and molecular dynamics simulations. *Int J Mater Res* **99**(10): 1136–1143 (2008)
- [112] Pastewka L, Moser S, Moseler M. Atomistic insights into the running-in, lubrication, and failure of hydrogenated diamond-like carbon coatings. *Tribol Lett* **39**(1): 49–61 (2010)
- [113] Dag S, Ciraci S. Atomic scale study of superlow friction between hydrogenated diamond surfaces. *Phys Rev B* **70**(24): 241401 (2004)
- [114] Eryilmaz O L, Erdemir A. On the hydrogen lubrication mechanism(s) of DLC films: An imaging TOF-SIMS study. *Surf Coat Technol* **203**(5–7): 750–755 (2008)
- [115] Shi J, Wang Y F, Gong Z B, Zhang B, Wang C B, Zhang J Y. Nanocrystalline graphite formed at fullerene-like carbon film frictional interface. *Adv Mater Interfaces* **4**(8): 1601113 (2017)

Qingyuan YU. He obtained his bachelor degree in 2018 from Southwest Jiaotong University. Then he became a Ph.D. candidate under

the supervisor of Prof. Zhang at the State Key Laboratory of Tribology (SKLT), Tsinghua University. His research interests include coating technology and the mechanisms of solid superlubricity.

Xinchun CHEN. He received his Ph.D. degree in mechanical engineering from The University of Tokyo, Japan, in 2014. Then he joined the SKLT at Tsinghua

University. His current position is an associate professor of the SKLT. His research areas cover the coating technology, tribology of solid lubricants, nanomaterials, superlubricity, and surface and interface phenomena.

Chenhui ZHANG. He received his Ph.D. degree in mechanical engineering from Tsinghua University, Beijing, China in 2004. Then he has been working at the SKLT of Tsinghua University. From February 2011 to August 2011, he was invited

to Luleå University of Technology in Sweden as a visiting scholar. He was also invited to Weizmann Institute of Science in Israel as a visiting scientist from February 2012 to January 2013. Currently, he is a professor at Tsinghua University. His research interests are superlubricity, water based lubrication, and coating technology.