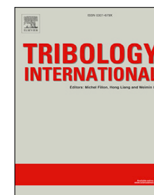
Tribology International 117 (2018) 107–111

Contents lists available at ScienceDirect

Tribology International

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



Bias voltage dependence of superlubricity lifetime of hydrogenated amorphous carbon films in high vacuum

Longchen Cui [a], Hui Zhou [a,*], Kaifeng Zhang [a], Zhibin Lu [b], Xianrong Wang [a]

[a] Science and Technology on Vacuum Technology and Physics Laboratory, Lanzhou Institute of Physics, Lanzhou 730000, China
[b] State Key Laboratory of Solid Lubrication, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, China

ARTICLE INFO

Keywords:
Polymer-like carbon film
Reactive magnetron sputtering
Superlubricity
Bias voltage

ABSTRACT

We deposit hydrogenated amorphous carbon (a-C:H) films by magnetron sputtering of graphite in an Ar + C_2H_2 mixture at various bias voltages. The mechanical properties, Raman spectra, and high-vacuum frictional behaviors of the a-C:H films indicate that the films deposited at bias 0, –50, and −100 V are polymer-like carbon (PLC) films and the film deposited at −150 V is a diamond-like carbon (DLC) film. The lifetimes of superlubricity, with friction coefficient ~0.002, of the PLC films in high-vacuum increase from 10000 to 28000 cycles with increasing bias, although the film thicknesses decrease. The DLC film's wear-life is ~600 cycles. The enhanced wear-resistance in PLC films is attributed to improvement of the crosslinking degree of the PLC network and the film compactness.

1. Introduction

Hydrogenated amorphous carbon (a-C:H) films have been deemed as promising solid lubricating materials for space applications due to their superlubricity (friction coefficients below 0.01) performances in high vacuum [1–7]. However, only the films with sufficient H content (above a threshold of ~40 at.%), called polymer-like carbon (PLC) films, can yield long lifetime of superlubricity in vacuum until the film is worn out [3–6]. As for the diamond-like carbon (DLC) films with relatively low H content, the superlubricity is transient and then the friction coefficients fluctuate at high values above 0.5 [1,3,4,7]. The exodiffusion of limited unbonded H within the DLC network to the wearing surface is crucial to maintain its transient superlubricity in vacuum, yet sufficient bonded H enables the PLC network superlubricating inherently [3,5]. Thus, the lifetime of superlubricity is shorter than (equal to) the lifetime of DLC (PLC) film in high vacuum [1,5,7].

To deposit PLC films, controlling the energy of $C_mH_n^+$ ions in plasma at a low level is pivotal [8]. With the increase of $C_mH_n^+$ energy, the H content of the a-C:H film lowers and the film evolves into a DLC [8,9]. In practice, PLC films are usually deposited on substrates that are applied no or low additional negative bias voltages by inductively coupled plasma discharge [5,10], reactive magnetron sputtering [6,11], etc. Moreover, the H/C ratio of the hydrocarbon precursor is not a decisive factor affecting the H content of the deposited a-C:H film. Acetylene (C_2H_2) [4] and benzene (C_6H_6) [9] with a low H/C ratio can also be polymerized in plasma to form a-C:H films with H contents as high as 50 at.% at low negative bias voltages. Liu et al. [6] showed that the Si-Al co-doped PLC film deposited without applying bias voltage exhibited long superlubricity lifetime (>15000 cycles) in vacuum. Vanhulsel et al. [5] reported that the superlubricity lifetimes of PLC films deposited at bipolar pulsed bias voltages in range of 75–120 V (the pulse frequency and the duty cycle were also varied) were widely different (41000, 100000, and 6500 cycles). However, the correlation between bias voltages and superlubricity lifetimes of the PLC films in high vacuum was not disclosed [5]. Although exerting negative bias voltage lowers the H amount within the a-C:H network [9], it enhances the ion bombardment effects during film growing that makes the film more compact and resistant to wear [12–14]. Therefore, there probably is an optimal negative bias voltage in low value range, not zero, for the superlubricity lifetime of a-C:H films in high vacuum for a certain deposition method.

With these perspectives in mind, in this study, we deposit a-C:H films by reactive magnetron sputtering of graphite target in argon (Ar) and C_2H_2 mixture at various bias voltages of 0, –50, −100, and −150 V. The effect of bias voltages on the superlubricity lifetimes of a-C:H films in high vacuum is first investigated.

* Corresponding author.
E-mail address: zhouhui510@sina.com (H. Zhou).

http://dx.doi.org/10.1016/j.triboint.2017.08.020
Received 18 May 2017; Received in revised form 23 July 2017; Accepted 22 August 2017
Available online 24 August 2017
0301-679X/© 2017 Published by Elsevier Ltd.

2. Experimental details

2.1. Film deposition

The substrate material used was p-type silicon (100) wafers 430 μm in thickness and 50.8 mm diameter. The substrate was vertically hung on a stainless steel holder, which was rotating at 3 rpm during the deposition process, at the center of a vacuum chamber by a stainless steel clamp. The distance between the wafer and the target is ~40 cm. A small surface area at the edge of each wafer was masked to form a step for subsequent film thickness measurement. The base pressure in the chamber was about 2×10^{-4} Pa. Before film deposition, the Si wafers were cleaned by Ar ion bombardment to improve adhesion of the a-C:H films, generated by an ion source in Ar atmosphere (~0.1 Pa), at bias voltage of −500 V for 20 min. Then, a-C:H films were deposited by magnetron sputtering of graphite target in a mixture of Ar and C_2H_2 with flow rate of 10 and 50 sccm, respectively, at various bias voltages of 0, –50, −100, and −150 V. The gas pressure during deposition was about 0.5 Pa. Both the graphite target and the bias voltage were controlled by direct-current pulse power supplies with frequency of 40 kHz. The target current was set as 1.5 A, and the duty cycle was 25%. The duty cycle of bias voltage was fixed as 40%. The target current and gas flow rates had been optimized (unpublished). The duration of the film deposition was 2.0 h. The chamber and substrates were not heated intentionally, and the temperature in the chamber was measured between 18 and 30 °C during all the depositions.

2.2. Film characterization

An optical profilometer (Taylor Hobson) was used to measure the thickness and surface roughness of the a-C:H film. A nanoindenter (Anton Parr), equipped with a Berkovich diamond tip, was used to determine the nanohardness and elastic modulus of the a-C:H film. The indentation depth was controlled to less than 10% of the film thickness to minimize the substrate contribution, and the average values of 9 replicate indentations on each film were reported in Fig. 1. A Raman spectrometer (Horiba Scientific) with a laser excitation wavelength of 532 nm was used to examine the bonded H content of the a-C:H films.

Unidirectional sliding friction tests in high vacuum with residue pressure lower than 2×10^{-4} Pa were performed on a ball-on-disk tribometer (CSM Instruments). The high vacuum is obtained with a turbo-molecular pump and the chamber is sealed by rubber gaskets. The mating pair was a commercially available 9Cr18 steel ball, 8.0 mm in diameter, with a hardness of about 8.4 GPa and a surface roughness R_a lower than 20 nm. The normal load applied by a dead weight was 5.0 N, and the corresponding initial maximum Hertzian contact pressure of ~840 MPa. The rotational frequency was set as 500 rpm, and the rotational radius was 10 mm. The corresponding linear speed was ~0.524 m/s. The friction force was measured by a strain force transducer with resolution of 30 μN. The tests were stopped until the friction coefficient exceeded 0.3.

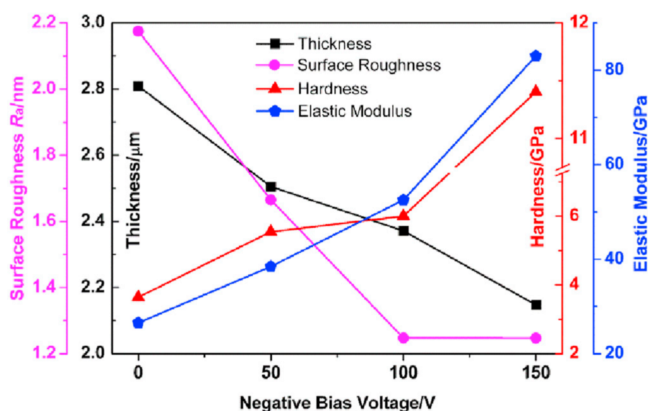


Fig. 1. The variations of the thickness, surface roughness, nanohardness and elastic modulus of the a-C:H films with the substrate negative bias voltage.

3. Results and discussion

3.1. Bias voltage dependence of thickness, surface roughness, and mechanical properties of a-C:H films

Fig. 1 shows the variations of the thickness, surface roughness, nanohardness and elastic modulus of the as-deposited a-C:H films with the negative bias voltage on the substrate. The film thickness exhibits a decrease from 2.81 to 2.15 μm with increasing negative bias voltage from 0 to 150 V. This is due to the increased ion bombardment of the growing film with a higher energy flux at a higher bias voltage, resulting in a lower deposition rate. The energetic Ar^+ ion impingement preferentially removes the poorly adherent atoms and particles, enhances the surface mobility of adatoms to more stable positions (generally from crests to valleys) to lower surface energy, and leads to the elimination of cavities in the films [12–14]. Besides, the dominant growth mechanism of a-C:H films will shift from *surface absorption* to *subplantation* with the increase of ion energy [8,15]. In *surface absorption*, the C_mH_n radicals and ions with low energy just stick to the growing surface, which could create many nanoholes in the film [16] due to the steric hindrance effect. The existence of nanoholes in PLC films has been shown by Erdemir et al. by a molecular dynamics simulation [17]. In *subplantation*, however, the energetic $C_mH_n^+$ ions can penetrate the surface into subsurface interstitial sites, which makes the film structure much denser [15]. Consequently, the a-C:H film deposited at a high bias voltage is thinner but would smoother and more compact than the non-/low-biased film. The augment of film compactness is corroborated by the decrease of surface roughness [16] R_a from 2.17 to 1.25 nm as the negative bias increases from 0 to 100 V (The R_a of the uncoated Si wafer was measured to be ~0.8 nm). The surface roughness of the a-C:H film deposited at bias voltage of −150 V is almost the same as that of the film at bias −100 V. It is reported that surface roughness of amorphous carbon films decreases firstly and then increases with the increase of bias voltage [18–20]. Hence, we can deduce that the surface roughness of the a-C:H film should reach its minimum at bias between −100 and −150 V. Roughening at a higher bias voltage is due to the excessive resputtering and irradiation damage [20].

Both the nanohardness and elastic modulus of the a-C:H films increase with the bias voltage, and the increase is more notable in bias voltage range of −100 to −150 V. The films synthetized at bias voltages of 0, −50, and −100 V are relatively soft, with the values of hardness in range of 3.6–6.0 GPa, in the a-C:H family. However, the hardness soars to 11.4 GPa at bias voltages of −150 V, indicating a significant change in bias voltage range of −100 to −150 V in terms of film deposition mechanism and properties. Generally, the mechanical strength of the a-C:H film increases with the decreases of the bonded H content or the fraction of polymeric C–H bonds. A lower bonded H content means a higher crosslinking degree and thus rigidity of the a-C:H network [21]. As stated above, when the energy of $C_mH_n^+$ ions is low, the dominant growth mechanism is *surface absorption*, in which C_mH_n species just adhere on the growing surface without breaking many C–H bonds [22]. With increase of ion energy, the *subplantation* gradually takes over the growth, in which displacement of H from subsurface C–H bonds by $C_mH_n^+$ ions is the dominant event [8], leading to a lower C–H fraction. The decrease of the C–H fractions with increasing bias voltages is verified by Raman spectra as shown below. Besides, the enhanced compactness (i.e., reduction of nanovoids in the film) contributes to the higher mechanical strength of the film grown at a higher bias voltage as well.

3.2. Bias voltage dependence of the bonded H content in a-C:H films

As shown in Fig. 2a., the films deposited at bias voltages of 0, –50, and

Download English Version:

https://daneshyari.com/en/article/4985749

Download Persian Version:

https://daneshyari.com/article/4985749

Daneshyari.com