Applied Surface Science 422 (2017) 147–154

Contents lists available at ScienceDirect

Applied Surface Science

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

Full Length Article

Friction and wear of hydrogenated and hydrogen-free diamond-like carbon films: Relative humidity dependent character

Jing Shi [a,b], Zhenbin Gong [a,b], Yongfu Wang [a,b], Kaixiong Gao [a], Junyan Zhang [a,*]

[a] State Key Laboratory of Solid Lubrication, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, China
[b] University of Chinese Academy of Sciences, Beijing 100049, China

ARTICLE INFO

Article history:
Received 7 December 2016
Received in revised form 24 May 2017
Accepted 24 May 2017
Available online 27 May 2017

Keywords:
Diamond like carbon
Relative humidity
Friction
Capillary force
Tribofilm

ABSTRACT

In this study, tribological properties of hydrogenated and hydrogen free diamond-like carbon films at various relative humidity (RH) were investigated to understand the friction mechanism in the presence of water molecules. At normal load of 2N, DLC-H film's friction coefficient was 0.06 at RH14% while DLC film's friction coefficient was 0.19 at RH17%. With the increase of RH, their friction coefficient converged to about 0.15. This character remained unaltered when the normal load was 5N. Results show that low friction of DLC-H film at low RH was attributed to the low shear force aroused by graphitic tribofilm at wear care center. However, the high friction of DLC film was mainly endowed by the high adhesive force aroused by σ dangling bonds. At high RH, solid-to-solid contact was isolated by water molecules confined between the counterfaces, where capillary was a dominant factor for friction. In addition to the capillary force, the absence of tribofilm was also accountable. These two factors lead to the level off of friction coefficient for DLC-H and DLC films. Moreover, for both DLC-H and DLC films, tribo-oxidization was proved to be closely related to wear rate with the assist of H_2O molecules during sliding.

1. Introduction

Diamond like carbon (DLC) films with unique physical, mechanical and tribological properties have been serving as one of the most promising solid lubricants since 1980s [1–4]. However, their tribological properties are found to be strongly affected by external stimulis, such as relative humidity, vacuum pressure and gas atmospheres [5,6]. For instance, hydrogenated DLC films had coefficient (Cof.) below 0.01 in vacuum, and increased linearly to 0.07 when water vapor was added, but tetrahedral amorphous carbon (ta-C) film exhibited high friction Cof. and severe wear in dry air and vacuum [7–9]. Similar observation was found for the hydrogenated fullerene-like carbon films [10]. Furthermore, it was noticed that when considering the DLC films coated on mechanical parts worked in humid air or water environments, their application was severely restricted. Therefore, investigations on the DLC films' hydrophobicity could provide opportunities for its potential applications in fields of moisture-proof lubricants, water-proof materials, electrodes and anticorrosive materials [11–13]. In other words, it is of concurrent significance to investigate the effect of various relative humidity on tribological properties of DLC films. Also, insights into DLC film's friction mechanism in the presence of water and discussions about the synergetic factors on its tribological properties could expand the application in water-based environments. In this study, friction and wear behaviors linked with interfacial states were examined as a function of monovariate relative humidity at different applied normal forces to probe the intrinsic solid contact and water molecule effect.

According to the passivation mechanism [9,14], sliding produced dangling bonds would be terminated by —H or —OH from the humid atmosphere or other available environmental species. This is usually a relative humidity dependent character. In addition to the passivation mechanism, rehybridization theory suggests a 'graphitic' layer with sp^2 carbon rich character would be formed at frictional interface [15]. However, it was also revealed that besides these two factors, capillary force generated friction at multi-asperities contact should not be overlooked [16–18]. It was reported that the presence of water was associated with DLC film's friction and wear, and attributed differently in various relative humidity ranges [2,19,20]. Here in this study, compared with hydrogenated DLC films, hydrogen free DLC film's low friction was more count upon the presence of H_2O molecules. Intrinsic hydrogen was essential to achieve low friction at low RH, while the capillary force determined by surface energy was the dominant factor at high RH. It was revealed that the measured interfacial friction was generated by direct counterface contact and water molecules confined

* Corresponding author.
E-mail addresses: junyanzhang@licp.cas.cn, shijing@licp.cas.cn (J. Zhang).

http://dx.doi.org/10.1016/j.apsusc.2017.05.210
0169-4332/

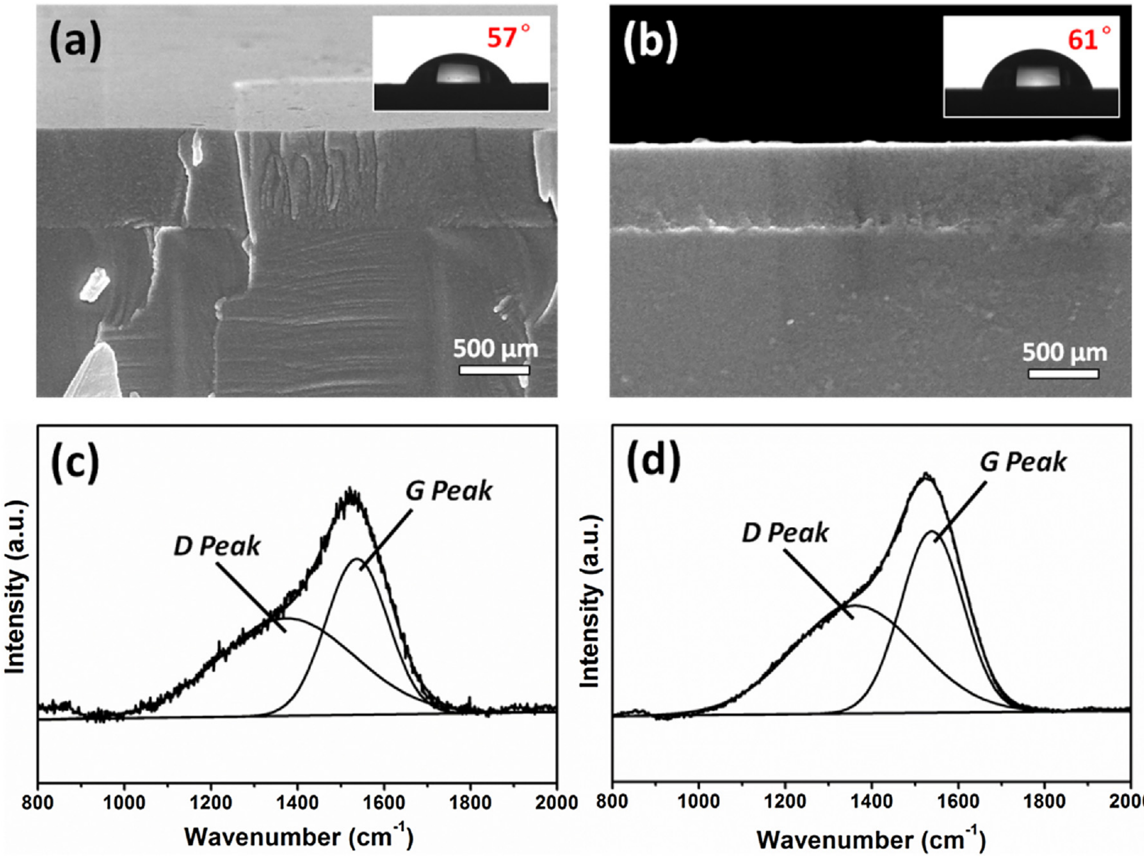

Fig. 1. Sectional scanning electron microscope images of (a) DLC-H film and (b) DLC film, the insets are their corresponding contact angle with pure water. Raman spectra of (c) DLC-H film and (d) DLC film from wavenumber 800 cm^{-1} to 2000 cm^{-1} and the Gassian fitting results.

between them in a synergetic mode. The authors expect the results and discussions could encourage considerations on producing a novel carbon based solid lubricant with excellent environmental insensitivity.

2. Materials and methods

2.1. Films reparation and intrinsic properties

The hydrogenated diamond-like carbon (DLC-H) films were prepared from CH_4 and Ar gas mixture in a plasma discharging system. The details about this system could be found in our previous study [21]. The deposition parameters are as follows: (a) flow rate of CH_4/Ar was 20 sccm/200 sccm, (b) substrates placed on negative pole were supplied with negative bias power source (bias voltage was −1100 V), (c) power frequency was 70KHz and duty cycle was 70%, and (d) the deposition pressure was kept constant at 17 Pa. Contrastive hydrogen free diamond-like carbon (DLC) films were deposited via magnetron sputtering method [22] using graphite target (99.99% purity) as carbon source and Ar gas (∼250 sccm). The cathodic graphite target was supplied with direct current pulsed power (with voltage of 370 V) after the vacuum chamber was pumped to 1.0×10^{-4} Pa. During the deposition, the current was kept constant at 2A, which requires a fine adjustment of Ar gas flow rate. Deposition pressure was 0.8 Pa. Both the DLC-H and DLC films were deposited on pre-cleaned commercial p-type mono-crystalline Si (111) wafers. Films sectional morphology and thickness were observed by scanning electron microscope (SEM, JSM-5601LV).

2.2. Friction and wear properties analyzing methods

A ball-on-disk tribometer was employed to perform the friction tests. The tribometer was placed in a chamber connected with a humidity control system. The Al_2O_3 counterpart ball with 5 mm diameter was sliding against the pristine films with a rotational speed of 100 rounds per minute and rotation radius of 3 mm under normal load of 2N and 5N. All the tests were performed for 6000 cycles, and all the films were not ruptured after the friction. The same friction tests were performed at least three times and the reproducibility of friction coefficient was never worse than ±0.008. Film's contact angle was measured by a contact angle meter (DSA100) at ambient temperature. The contact angle images were taken after the distilled water dropped onto the film surface. Contact angle of each sample was tested for five times to get an average value. Optical microscope (Olympus, DP73), micro-Raman (LabRam HR800, laser wavelength of 532 nm), and X-ray photoelectron spectroscopy (XPS, PHI-570) were employed to investigate the film and the contact area interface morphology, structure and chemical composition before and after the friction. The wear track cross section profile was measured by two-mode three-dimensional surface contour graph (AEP) after 6000 sliding cycles.

3. Results and discussions

3.1. Intrinsic character and tribological behaviors of DLCs

Hydrogenated and hydrogen free DLC films deposited on silicon substrates are ∼743 nm and 658 nm in thickness, respectively (Fig. 1a and b). The wettability of DLC films is a crucial parameter for its tribological properties at boundary lubrication. It determines the